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Synthesis of multivalent *S*-glycosides analogs of a heparan sulfate sequence

Dindet Steve-Evanes Koffi Teki,[a,b] Abed Bil,[b] Vincent Moreau,[b] Vincent Chagnault,*[b] Bamba Fanté,[a] Ané Adjou[a] and José Kovensky*[b]

Supporting information

Contents

Experimental part

General Methods

All reagent-grade chemicals were obtained from commercial suppliers and were used as received. Characterizations of known compounds were in accordance with literature. Optical rotations were recorded in CH_2Cl_2 solution. FTIR spectra were obtained using ATR and are reported in cm^{-1}. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in D_2O, DMSO, MeOD or $CDCl_3$. The proton and carbon signal assignments were determined from decoupling experiments, COSY, HSQC, HMBC, ROESY, TOCSY spectra. TLC were performed on Silica F254 and detection by UV light at 254 nm or by charring with cerium molybdate reagent. Column chromatography was performed on Silica Gel 60 (230 mesh). High-resolution electrospray mass spectra in the positive ion mode were obtained on a Q-TOF Ultima Global hybrid quadrupole/time-of-flight instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source and an additional sprayer (Lock Spray) for the reference compound. The source and desolvation temperatures were kept at 80 and 150 °C, respectively. Nitrogen was used as the drying and nebulizing gas at flow rates of 350 and 50 L/h, respectively. The capillary voltage was 3.5 kV, the cone voltage 100 V and the RF lens1 energy was optimized for each sample (40 V). For collision-induced dissociation (CID) experiments, argon was used as collision gas at an indicated analyser pressure of 5.10^{-5} Torr and the collision energy was optimized for each parent ion (50-110 V). Lock mass correction, using appropriate cluster ions of sodium iodide $(NaI)_nNa^+$, was applied for accurate mass measurements. The mass range was typically 50-2050 Da and spectra were recorded at 2 s/scan in the profile mode at a resolution of 10000 (FWMH).

Synthesis of compound 2.

To a solution of methyl 1,2,3,4-tetra-*O*-acetyl-D-glucopyranuronate **16** (2.13 g; 5.664 mmol) in DCM (26 mL), was added HBr dropwise (20 mL; 33 % in acetic acid; 113.3 mmol) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 20 min. and then at room temperature. After 8 h, the mixture was washed 3 times with water containing crushed ice, then with a saturated solution of $NaHCO_3$ (at 0 °C) and finally with ice water. The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated. The desired product **2** was obtained as white crystals (1.96 g; 88 %). Rf: 0.64 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 82 °C; literature[1]: 82 - 84 °C; $[\alpha]_D^{20}$: +201.8 (c = 0.5 DCM); literature[1]: +198 ($CHCl_3$); IR (ATR): 1747.5; 1377.2; 1219; 1111; 1047.4 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, *J* = 4.0 Hz, 1H, H_1); 5.61 (t, *J* = 9.7 Hz, 1H, H_3'); 5.23 (dd, *J* = 10.3, 9.5 Hz, 1H, H_2); 4.85 (dd, *J* = 10.0, 4.0 Hz, 1H, H_4); 4.57 (dd, *J* = 10.3, 0.7 Hz, 1H, H_5); 3.76 (s, 3H, -COOC$\underline{H}_3$); 2.09 – 2.04 (s, 9H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 –169.6 (3 x $CH_3\underline{C}O$-); 166.8 (-$\underline{C}OOCH_3$); 85.5 (C_1); 72.2 (C_5); 70.5 (C_4); 69.4 (C_3); 68.6 (C_2); 53.3 (-COO$\underline{C}H_3$); 20.7 –20.6 (3 x $\underline{C}H_3COO$-).

Synthesis of compound 4

To a solution of compound **12** (0.080 g; 0.159 mmol) at 0.15 M in dimethylacetamide (DMA) (1.06 ml) was added dithiothreitol (0.049 g; 0.318 mmol) and $NaHCO_3$ (1.33 mg; 0.0159 mmol) under an argon atmosphere. The reaction mixture was stirred at 33 °C until a total conversion was reached (24 h). The mixture was dissolved in ethyl acetate (50 mL) and was washed several times with a saturated solution of NaCl (50 mL). The organic layer was then dried over sodium sulfate, filtered and concentrated. The residue was purified by flash chromatography over silica gel (cyclohexane / ethyl acetate; 50/50) to lead to yellow crystals of the desired product **4** (0.055 g; 76 %). Rf: 0.61 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 42-44 °C; $[\alpha]_D^{20}$: +129.2 (c = 0.5 DCM); IR (ATR): 1724.4; 1452.4; 1273; 1097.5; 1070.5; 1030; 709.8 cm^{-1}; HRMS: Calcd. for $[C_{23}H_{24}O_8NaS]$: m/z 483.1090 $[M+Na]^+$; Found 483.1081 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.97 (m, 2H, H_{aro}); 7.98 – 7.89 (m, 2H, H_{aro}); 7.56 – 7.45 (m, 2H, H_{aro}); 7.43 – 7.28 (m, 4H, H_{aro}); 5.78 (ddd, *J* = 10.7, 8.4, 1.0 Hz, 1H, H_3); 5.17 (d, *J* = 8.5 Hz, 2H, H_1, H_2); 4.54 (t, *J* = 3.0 Hz, 2H, H_6, H_6); 4.01 (ddd, *J* = 10.8, 4.1, 2.7 Hz, 1H, H_5); 3.43 (s, 3H, -OC$\underline{H}_3$); 3.14 (td, *J* = 10.8, 9.6 Hz, 1H, H_4); 2.16 (s, 3H, C$\underline{H}_3$CO-); 1.63 (d, *J* = 9.5 Hz, 1H, -SH). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8 ($CH_3\underline{C}O$-); 166.1 – 166.0 (-O$\underline{C}$OBz); 133.5 – 128.5 (12 C_{aro}); 97.5 (C_1); 72.9 (C_2); 72.8 (C_3) 71.6 (C_5); 63.8 (C_6); 55.7 (-O$\underline{C}H_3$); 41.1 (C_4); 21.0 ($\underline{C}H_3$CO-).

Synthesis of compound 5

To a solution of **15** (1 g; 2.11 mmol) in a mixture of DCM / H_2O (30 mL; 2 / 1; v / v), was added sodium metabisulfite (1.2 g; 6.34 mmol). The mixture was stirred at reflux for 6 h under an argon atmosphere. Then the reaction was cooled at room temperature and the products were extracted with DCM (3 x 50 mL). The organic phases were combined and washed with water, dried over sodium sulfate, filtered and concentrated. The desired compound **5** was purified over silica gel chromatography (cyclohexane / Ethyl acetate; 60 / 40; v / v) to lead to white crystals (0.53 g; 73 %). Rf: 0.37 (cyclohexane / Ethyl acetate; 60 / 40; v / v); MP: 136-138 °C; literature[2]: 125 °C; $[\alpha]_D^{20}$: +1.8 (c = 0.5 DCM); literature[3]: -2.77 (c = 0.94 $CHCl_3$); IR (ATR): 1479.4; 1375.25; 1213.2; 1082.1; 1058.9; 1037.7 cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$): δ 5.19 – 5.15 (m, 2H, H_3, H_4); 4.98 – 4.86 (m, 1H, H_2); 4.51 (t, J = 9.9 Hz, 1H, H_1); 4.03 – 3.95 (m, 1H, H_5); 3.69 (s, 3H, -COOC$\underline{H}_3$); 2.32 (d, J = 10.1 Hz, 1H, S$\underline{H}$); 2.01 – 1.96 (3s, 9H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0 – 169.3 ($CH_3\underline{C}O$-); 166.7 (-$\underline{C}OOCH_3$); 79.0 (C_1); 76.6 (C_5); 73.3 (C_2); 72.8 (C_4); 69.3 (C_3); 53.0 (-COO$\underline{C}H_3$); 20.7 – 20.5 ($\underline{C}H_3$CO-). NMR data were in agreement with the literature.[2]

Synthesis of compound 6

To a solution of 6-*O*-acetyl-2,3-di-*O*-benzoyl-α-D-galactopyranoside **11** (0.2 g; 0.45 mmol) in anhydrous DCM (10 mL) under an argon atmosphere, was added successively anhydrous pyridine (0.15mL; 0.112 mmol) and triflic anhydride (0.189 ml; 0.9 mmol) dropwise at -5 °C. After 4 hours of stirring, the temperature was brought back to room temperature and the reaction mixture diluted with DCM (50 mL). The mixture was washed several times with a saturated solution of $NaHCO_3$ and with a saturated solution of NaCl. Then the organic phase was dried over sodium sulfate, filtered and concentrated to afford brown crystals (0.25 g; 98 %) which have been used without further purification. Rf: 0.62 (cyclohexane / Ethyl acetate; 70 / 30; v / v); MP: 43-45 °C; $[\alpha]_D^{20}$: +115.2 (c = 0.5 DCM); IR (ATR): 1730.2; 1413.8; 1244.1; 1213.2; 1141.9; 1116.8; 1091.7; 1030; 914.3; 711.7 cm^{-1}; HRMS: Calcd. for [$C_{24}H_{23}O_{11}F_3NaS$]: m/z 599.0811 [M+Na]$^+$; Found 599.0816 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (ddt, *J* = 30.4, 7.1, 1.4 Hz, 4H, H_{aro}); 7.60 – 7.47 (m, 2H, H_{aro}); 7.38 (dt, *J* = 10.6, 7.8 Hz, 4H, H_{aro}); 5.89 (dd, *J* = 10.8, 2.9 Hz, 1H, H_3); 5.56 (dd, *J* = 10.8, 3.6 Hz, 1H, H_2); 5.51 (d, *J* = 2.9 Hz, 1H, H_4); 5.25 (d, *J* = 3.6 Hz, 1H, H_1); 4.43 (t, *J* = 6.8 Hz, 1H, H_5); 4.36 (dd, *J* = 11.2, 6.4 Hz, 1H, H_6); 4.14 (dd, *J* = 11.2, 7.2 Hz, 1H, H_6); 3.46 (s, 3H, -OC$\underline{H}_3$); 2.11 (s, 3H, $\underline{C}H_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3 (CH_3CO-); 165.9 – 165.8 (-O$\underline{C}$OBz); 133.9 – 128.5 (C_{aro}); 120.0 (-S$\underline{C}F_3$); 97.5 (C_1); 82.9 (C_4); 68.2 (C_2); 67.6 (C_3); 65.8 (C_5); 61.2 (C_6); 56.2 (-O$\underline{C}H_3$); 20.7 ($\underline{C}H_3$CO-).

Synthesis of compound 8

In a 250 mL round bottom flask containing anhydrous acetonitrile (100 mL), were added successively the methyl-α-D-galactopyranoside (5 g; 25.75 mmol), benzaldehyde dimethyl acetal (5.88 g; 1.5 eq.; 38.62 mmol) and anhydrous iron (III) chloride (0.83 g; 0.2 eq.; 5.15 mmol). Then the reaction mixture was stirred at room temperature under an argon atmosphere. After 4 h of stirring, the solvent was evaporated. The residue was then diluted in a saturated solution of $NaHCO_3$ (50 mL) and the aqueous phase extracted with DCM (3x50 mL). The combined organic phases were dried over magnesium sulfate, filtered and concentrated. The residue was washed several times with a mixture cyclohexane/EtOAc (95/5; v/v). White crystals were obtained (8.9 g; 86 %). Rf: 0.45 (DCM / MeOH; 95/5). MP: 164-166 °C. $[\alpha]_D^{20}$: +141.6 (c = 0.5 DCM). IR (ATR): 3471.9; 1452.4; 1367.5; 1143.8; 1082.1; 1033.9; 999.1; 983.7; 788.9; 773.5; 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 - 7.42 (m, 2H, H_{aro}); 7.41 – 7.27 (m, 3H, H_{aro}); 5.51 (s, 1H, PhC$\underline{H}$-); 4.88 (d, *J* = 2.9 Hz, 1H, H_1); 4.25 (dd, *J* = 12.6, 1.6 Hz, 1H, H_6); 4.21 – 4.18 (m, 1H, H_4); 4.03 (dd, *J* = 12.6, 1.8 Hz, 1H, H_6); 3.94 – 3.84 (m, 2H, H_2, H_3); 3.63 (d, *J* = 1.6 Hz, 1H, H_5); 3.42 (s, 3H, -OC$\underline{H}_3$); 2.84 (s, 1H, OH); 2.65 (s, 1H, OH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 – 126.4 (C_{aro}); 101.3 (Ph$\underline{C}$H-); 100.4 (C_1); 76.0 (C_4); 69.8 (C_3); 69.70 (C_2); 69.4 (C_6); 62.8 (C_5); 55.8 (-O$\underline{C}H_3$).

Synthesis of compound 9

In a round bottom flask was added pyridine (150 mL) and the solvent was cooled at 0 °C using an ice bath. Methyl 4.6-*O*-benzylidene-α-D-galactopyranoside **8** (5 g; 17.72 mmol) and benzoyl chloride (8.64 mL; 4.2 eq.; 74.44 mmol) were successively added and the reaction mixture was stirred at 0 °C under an argon atmosphere for 3 h. Then methanol (8 mL) was added dropwise and the mixture was neutralized using a saturated solution of $NaHCO_3$ (100 mL). The resulting aqueous phase was then extracted with DCM, and the combined organic phases dried over magnesium sulfate, filtered and evaporated under reduce pressure. The desired product was purified over silica gel chromatography (cyclohexane/EtOAc; 80/20; v/v). White crystals were obtained (7.73 g; 89 %). Rf: 0.14 (cyclohexane/EtOAc; 80/20; v/v). MP: 192-194 °C. $[\alpha]_D^{20}$: +213.7 (c = 0.75 $CHCl_3$). IR (ATR): 1728; 1452.4; 1357.9; 1255.7; 1276.9; 1155.4; 1107.1; 1080.1; 1049.3; 1028.1; 977.9; 952.8; 785; 717.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (ddd, *J* = 8.5; 5.0; 1.4 Hz, 4H; H_{aro}); 7.58 – 7.45 (m, 4H, H_{aro}); 7.42 – 7.30 (m, 7H, H_{aro}); 5.80 – 5.75 (m, 2H; H_2, H_3); 5.58 (s, 1H, PhC$\underline{H}$-); 5.29 (d, *J* = 2.6 H,1H; H_1); 4.66 (dt, *J* = 2.4; 1.1 Hz, 1H; H_4); 4.36 (dd, *J* = 12.5; 1.6 Hz; 1H; H_6); 4.15 (dd, *J* = 12.5, 1.8 Hz, 1H, H_6); 3.91 (q, *J* = 1.6 Hz; 1H; H_5); 3.47 (s, 3H, -OC$\underline{H}_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3 – 166.1 (-O$\underline{C}$OBz); 137.7–126.3 (C_{aro}); 100.8 (Ph$\underline{C}$H-); 98.3 (C_1); 74.4 (C_4); 69.4 (C_2); 69.3 (C_6); 69.0 (C_3); 62.4 (C_5); 55.9 (-O$\underline{C}H_3$). NMR Analyses were in agreement with the literature.[4]

Synthesis of compound 10

To a mixture of DCM/MeOH (40 mL; 1/3; v/v) were added 2.3-di-*O*-benzoyl-4.6-*O*-benzylidene-α-D-galactopyranoside **9** (0.3 g; 0.612 mmol) and APTS monohydrate (270 mg; 2.35 eq.; 1.44 mmol). The reaction mixture was stirred at room temperature for 15 h and then quenched with pyridine (0.3 mL; 3.9 mmol). The solvent was evaporated under reduced pressure. The residue was purified over silica gel chromatography (cyclohexane/EtOAc;

50/50; v/v) to lead to pure white crystals of the desired product **10** (0.241 g; 98 %). Rf: 0.27 (cyclohexane / ethyl acetate 50/50) (v / v); MP: 59-61 °C; literature [5]: 95-96 °C; $[\alpha]_D^{20}$: +177.6 (c = 0.5 DCM); literature[5]: $[\alpha]_D^{21}$: +198 (c = 1.3 $CHCl_3$); IR (ATR): 3485.4; 1720.5; 1452.4; 1276.9; 1103.3; 1068.6; 1051.2; 1030; 711.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (td, *J* = 8.1, 1.4 Hz, 4H, H_{aro}); 7.56 – 7.44 (m, 2H, H_{aro}); 7.36 (t, *J* = 7.8 Hz, 4H, H_{aro}); 5.73 – 5.64 (m, 2H, H_2,H_3); 5.22 – 5.18 (m, 1H, H_1); 4.47 (q, *J* = 1.2 Hz, 1H, H_4); 4.17 – 3.77 (m, 3H, H_3, H_{6a}, H_{6b}); 3.43 (s, 3H, -OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3 – 166.0 (-O<u>C</u>OBz); 133.5 – 128.5 (C_{aro}); 97.9 (C_1); 71.1 (C_3); 69.9 (C_4); 69.1 (C_5); 69.1 (C_2); 63.4 (C_6); 55.7 (-O<u>C</u>H_3).

Synthesis of compound 11

To a solution of compound **10** (1 g; 2.48 mmol) in anhydrous acetonitrile (25 mL) was successively added triethyl orthoacetate (6.83 mL; 15 eq.; 37.31 mmol) and camphorsulfonic acid (0.18 g; 0.32 eq.; 0.789 mmol). The reaction mixture was stirred at room temperature for 30 min. and the solvent was then evaporated under reduced pressure. Acetonitrile (20 mL) and 90 % trifluoroacetic acid in water (2.28 mL) was added and the solution stirred for 5 min before to be diluted in toluene and concentrated. The obtained residue was then dissolved in DCM and washed with a saturated solution of $NaHCO_3$. The organic phase was the dried over sodium sulfate, filtered and concentrated. The crude reaction mixture was purified over silica gel chromatography (cyclohexane / ethyl acetate; v /v; 70 /30) to lead to white crystals of the desired compound **11** (0.78 g; 71 %). Rf: 0.33 (cyclohexane / ethyl acetate; v /v; 70 /30). MP: 44-46 °C. $[\alpha]_D^{20}$: +144.8 (c = 0.5 DCM). literature:[6] +232 (c = 1.2 $CHCl_3$); IR (ATR): 3504.7; 1720.5; 1452.4; 1271.1; 1103.3; 1070.5; 1049.3; 1031.1; 711.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (ddt, *J* = 7.1, 5.7, 1.4 Hz, 4H, H_{aro}); 7.58 – 7.44 (m, 2H, H_{aro}); 7.37 (td, *J* = 7.8, 3.9 Hz, 4H, H_{aro}); 5.68 (qd, *J* = 10.7, 3.2 Hz, 2H, H_2, H_3); 5.18 (d, *J* = 3.4 Hz, 1H, H_1); 4.41 (dd, *J* = 11.4, 5.9 Hz, 1H, H_6); 4.36 – 4.27 (m, 2H, H_6, H_4); 4.19 (t, *J* = 6.3 Hz, 1H, H_5); 3.44 (s, 3H, -O<u>C</u>H_3-); 2.58 – 2.48 (m, 1H, OH); 2.10 (s, 3H, C<u>H</u>$_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1 (-<u>C</u>OCH_3); 166.2 – 65.9 (-O<u>C</u>OBz); 133.5 –128.5 (12 C_{aro}); 97.7 (C_1); 70.8 (C_2); 68.8 (C_3); 68.1 (C_4); 67.5 (C_5); 62.9 (C_6); 55.5 (-O<u>C</u>H_3); 20.8 (<u>C</u>H_3CO-).

Synthesis of compound 12

To a solution of compound **6** (0.534 g; 0.926 mmol) in anhydrous DMF (10 mL) and under an argon atmosphere, was added potassium thioacetate (0.528 g; 4.63 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate (50 mL). The mixture was washed several times with a saturated solution of NaCl and water. The organic layer was then dried over sodium sulfate, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography over silica gel (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to yellow crystals of the desired product **12** (0.394 g; 85 %). Rf: 0.94 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 51-53 °C; $[\alpha]_D^{20}$: +150.2 (c = 0.5 DCM); IR (ATR): 1726.3; 1452.4; 1273; 1097.5; 1070.5; 1030; 711 cm^{-1}; HRMS: Calcd. for [$C_{25}H_{26}O_9NaS$]: m/z 525.1195 $[M+Na]^+$; Found 525.1201 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (ddd, J = 12.0, 7.8, 1.5 Hz, 4H, H_{aro}); 7.57 – 7.42 (m, 2H, H_{aro}); 7.36 (td, J = 7.7, 2.5 Hz, 4H, H_{aro}); 5.90 (m, 1H, H_3); 5.28 – 5.12 (m, 2H, H_1, H_2); 4.47 (dd, J = 12.2, 4.4 Hz, 1H, H_6); 4.24 (dd, J = 12.2, 1.8 Hz, 1H, H_6); 4.16 – 4.02 (m, 2H, H_5, H_4); 3.43 (s, 3H, -O<u>C</u>H_3); 2.21 (s, 3H, -SCO<u>C</u>H_3); 2.14 (s, 3H, -OCO<u>C</u>H_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8 (CH_3<u>C</u>OS-); 170.9 (CH_3<u>C</u>O-); 165.9 – 165.8 (-O<u>C</u>OBz); 133.5 –128.5 (12 C_{aro}); 97.4 (C_1); 73.2 (C_3); 69.3 (C_2); 68.7 (C_4); 63.3 (C_6); 55.8 (-O<u>C</u>H_3); 43.9 (C_5); 30.8 (<u>C</u>H_3COS-); 21.0 (<u>C</u>H_3CO-).

Synthesis of compounds 14

To a solution of sodium hydroxide (0.4 g; 113.56 mmol) in methanol (HPLC quality, 140 mL) was added glucurono-6,3-lactone **13** (20 g; 113.56 mmol). The solution was stirred at room temperature for 1 h and the solvent was then evaporated. The residue was diluted in pyridine (140 mL) and acetic anhydride (53.6 mL; 567.6 mmol) was added dropwise at 0 °C. After 4 h of stirring, the reaction mixture was evaporated and purified by silica gel chromatography (cyclohexane / ethyl acetate; 70 / 30; v / v). The fractions containing partially acetylated compounds were converted using the same contitions. Finally the desired compounds **14** was obtained as a mixture of α/β anomers (15/85 NMR ratio; 34 g; 80 %). The compound **14β** can be purified by recrystallization using a mixture of DCM / cyclohexane (5 / 95; v / v). Rf: 0.38 (cyclohexane / ethyl acetate; 60 / 40; v / v); Analyses for **14β** : MP: 171-173 °C; literature[7]: 175-177 °C; $[\alpha]_D^{20}$: + 24.0 (c = 0.5 DCM); literature[7]: + 8.6 (c =1 $CHCl_3$); IR (ATR): 2955; 1755.2; 1371.4; 1209.4; 1111; 1041.6 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (d, *J* = 7.7 Hz, 1H, H_1); 5.30 (t, *J* = 9.2 Hz, 1H, H_3); 5.24 (d, *J* = 9.4 Hz, 1H, H_4); 5.13 (dd, *J* = 8.9, 7.8 Hz, 1H, H_2); 4.17 (d, *J* = 9.5 Hz, 1H, H_5); 3.73 (s, 3H, -COOC<u>H</u>$_3$); 2.10 – 2.02 (3 s, 12H, C<u>H</u>$_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0 – 168.9 (4 x CH_3<u>C</u>O-); 166.9 (-<u>C</u>OOCH_3); 91.5 (C_1); 73.1 (C_5); 71.9 (C_3); 70.3 (C_4); 69.0 (C_2); 53.1 (-COO<u>C</u>H_3); 20.9 – 20.6 (4 x <u>C</u>H_3CO-). NMR data were in agreement with the literature.[7]

Synthesis of compound 15

To a solution of methyl 1-bromo-2,3,4-tri-*O*-acetyl-α-D-glucopyranuronate **2** (3.6 g; 9.06 mmol) in anhydrous acetone (25 mL), was added thiourea (2.6 g; 27.19 mmol). The reaction mixture was stirred at reflux for 2 h and then cooled at 4 °C overnight. A precipitate was obtained which was filtered and washed with cold and anhydrous acetone. The procedure was repeated with the filtrate until nothing more precipitates. The desired product **15** was obtained as white crystals (2.95 g; 69 %). Rf: 0.79 (DCM / MeOH; 95 / 5; v / v); MP: 179-181 °C; $[\alpha]_D^{20}$: + 0.2 (c = 0.5 H_2O); IR (ATR): 3267.4; 3172.9; 3062.9; 1656.85; 1417.7; 1373.3; 1246; 1226.7; 1091.7; 1039.6 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.59 (d, *J* = 10.0 Hz, 1H, H_1); 5.48 (t, *J* = 9.3 Hz, 1H, H_3); 5.30 – 5.16 (m, 2H, H_2, H_4); 4.52 (d, *J* = 10.0 Hz, 1H, H_5); 3.76 (s, 3H, -COOC$\underline{H}_3$); 2.18 – 2.05 (s, 9H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.1 – 170.9 (3 x $CH_3\underline{C}O$-); 169.3 (-S-$\underline{C}N_2H_4^+$); 168.5 (-$\underline{C}OOCH_3$); 82.3 (C_1; 76.6 (C_5); 73.3 (C_3); 70.1 (C_4); 70.1 ($C_{2'}$ 53.6 (-COO$\underline{C}H_3$); 20.4 (3 x $\underline{C}H_3$CO-).

Synthesis of compound 16

To a solution of **14** (1.4 g; 3.720 mmol) in anhydrous DMF (19 ml) was added hydrazine acetate (685 mg; 7.44 mmol) under an argon atmosphere. After 1 h of stirring at 20 °C, The solvent was evaporated and ethyl acetate (30 mL) was added. The reaction mixture was washed with a saturated solution of $NaHCO_3$ (3 x 30 ml) and a saturated solution of NaCl (10 ml). The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated. The desired compound **16** was obtained as a mixture of α/β anomers (80/20, NMR ratio) and as a yellow liquid (0.854 g; 69 %). Rf: 0.28 (cyclohexane / ethyl acetate; 50 / 50; v / v); ^1H NMR (400 MHz, $CDCl_3$) δ 5.57 – 5.45 (m, 2H, H_3, $H_{1\alpha}$); 5.16 – 5.07 (m, 1H, H_4); 4.93 – 4.80 (m, 1H, H_2); 4.55 (m, 2H, H_5); 3.70 (s, 3H, -COOC$\underline{H}_3$ α,β); 2.04-1.99 (9H, ($\underline{C}H_3$CO-). ^{13}C NMR (400 MHz, $CDCl_3$) δ 170.5 – 167.7 (8 x $CH_3\underline{C}O$-); 95.4 ($C_{1\beta}$); 90.2 ($C_{1\alpha}$); 72.8 ($C_{2\beta}$); 72.5 ($C_{3\beta}$); 71.7 ($C_{4\beta}$); 70.9 ($C_{2\alpha}$); 69.6 ($C_{4\alpha}$); 69.5 ($C_{5\beta}$); 69.2 ($C_{3\alpha}$) 70.0 ($C_{5\alpha}$); 53.0 (-COO$\underline{C}H_3$ α,β); 20.7 – 20.5 ($\underline{C}H_3$CO-). NMR data were in agreement with the literature[8].

Synthesis of compounds 17

To a solution of **5** (3.52 g; 10.06 mmol) in anhydrous DMF (53 mL) were successively added triethylamine (5.61 mL; 40.25 mmol) and dithiothreitol (1.21 g; 7.84 mmol) at -60 °C and under an argon atmosphere. The reaction mixture was stirred 5 min. and compound **6** (4.771 g; 8.275 mmol) was added dropwise. After 20 h of stirring at -60 °C, the solvent was evaporated and DCM (75 mL) was added. The solution was washed 2 times with an aqueous solution of HCl (5 %). The organic phase was separated and washed with a saturated solution of $NaHCO_3$ and then with water. The organic phase was dried over sodium sulfate, filtered and evaporated. The desired products **17** (5.073 g; 79 %; α/β: 80/20) was obtained as white crystals after purification over silica gel chromatography (cyclohexane / ethyl acetate; 60 / 40; v / v). The **17β**-anomer was isolated by recrystallization using methanol. **17β** analyses: Rf: 0.59 (cyclohexane / ethyl acetate; 60 / 40; v / v); MP: 155 °C; $[\alpha]_D^{20}$: +31.6 (c = 0.5 DCM); IR (ATR): 1743.7; 1452.4; 1369.5; 1247.9; 1224.8; 1107.1; 1051.2; 1033.9; 715.6 cm^{-1}; HRMS: Calcd. for [$C_{36}H_{40}O_{17}NaS$]: m/z 799.1884 [M+Na]$^+$; Found 799.1907 [M+Na]$^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 4H, H_{aro}); 7.54 – 7.49 (m, 2H, H_{aro}); 7.40 – 7.35 (m, 4H, H_{aro}); 5.98 (dd, *J* = 11.2, 9.6 Hz, 1H, H_3); 5.31 (dd, *J* = 9.6, 8.5 Hz, 1H, $H_{3'}$); 5.26 – 5.18 (m, 2H, H_2, H_4'); 5.17 – 5.12 (m, 1H, H_1); 5.04 (d, *J* = 10.1 Hz, 1H, $H_{1'}$); 4.93 (dd, *J* = 10.1, 8.9 Hz, 1H, $H_{2'}$); 4.58 (dd, *J* = 9.4, 3.0 Hz, 2H, H_6); 4.38 (ddd, *J* = 11.0, 3.8, 2.2 Hz, 1H, H_5); 4.15 (d, *J* = 9.9 Hz, 1H, $H_{5'}$); 3.75 (s, 3H,-COOC$\underline{H}_3$); 3.39 (s, 3H, -OC$\underline{H}_3$); 3.23 (t, *J* = 11.1 Hz, 1H, H_4) 2.14 – 1.55 (4s, 12H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6 – 166.5 (4 x $CH_3\underline{C}O$-); 165.8 (-$\underline{C}OOCH_3$); 165.7 – 133.5 (-O$\underline{C}$OBz); 133.4 – 128.5 (12 C_{aro}); 97.2 (C_1); 81.7 ($C_{1'}$); 75.5 ($C_{5'}$); 73.3 ($C_{3'}$, $C_{4'}$); 69.6 ($C_{2'}$); 69.1 (C_5); 69.0 (C_2); 67.3 (C_3); 63.5 (C_6); 55.4 (-O$\underline{C}H_3$); 53.0 (-COO$\underline{C}H_3$); 46.3 (C_4); 21.1 – 20.1 (4 x $\underline{C}H_3$CO-). **17α** analyses: ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.84 (m, 4H, H_{aro}); 7.56 – 7.42 (m, 2H, H_{aro}); 7.35 (dt, *J* = 14.0, 7.8 Hz, 4H, H_{aro}); 6.01 (dd, *J* = 10.8, 10.0 Hz, 1H, H_3); 5.79 (d, *J* = 5.4 Hz, 1H, $H_{1'}$); 5.21 – 5.12 (m, 2H, $H_{3'}$, H_1); 5.11 – 5.03 (m, 2H, $H_{4'}$, H_2); 4.88 (dd, *J* = 9.5, 5.4 Hz, 1H, $H_{2'}$); 4.65 – 4.53 (m, 2H, H_6, $H_{5'}$); 4.37 (dd, *J* = 12.1, 4.7 Hz, 1H, H_6); 4.02 (ddd, *J* = 11.3, 4.6, 2.2 Hz, 1H, H_5); 3.77 (s, 3H, -COOC$\underline{H}_3$); 3.41 (s, 3H, -OC$\underline{H}_3$); 3.36 (t, J = 11.0 Hz, 1H, H_4); 2.11, 2.02, 1.90, 1.66 (4s, 12H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8, 169.6, 169.5, 169.1 (4x$CH_3\underline{C}O$-); 167.7 (-$\underline{C}OOCH_3$); 165.9, 165.4 (-O$\underline{C}$OBz); 133.6 – 128.5 (12 C_{aro}); 97.2 (C_1); 83.5 ($C_{1'}$); 73.2 ($C_{4'}$) 72.5 (C_3); 69.7 ($C_{2'}$); 69.1 ($C_{5'}$); 69.0 (C_2, C_3); 68.5 (C_3); 63.5 (C_6); 55.8 (-O$\underline{C}H_3$); 53.0 (-COO$\underline{C}H_3$); 45.8 (C_4), 20.9 – 20.1 (4 x $\underline{C}H_3$CO-).

Synthesis of compounds 18

Compound **17β** (0.146 g; 0.187 mmol) was added in a round bottom flask placed in an ice bath. Then acetic anhydride (5.26 mL; 55.66 mmol), sulfuric acid (0.2 mL; 9.79 mmol) and acetic acid (2.3 mL; 0.041 mmol) were added successively. The reaction mixture was stirred for a few minutes at 0 °C followed by 3 h at room temperature. DCM (100 mL) was then added and the mixture was washed 2 times with ice-cold water, 3 times with a saturated solution of $NaHCO_3$ (100 mL) and with a saturated solution of NaCl (100 mL). The organic phase was then dried over sodium sulfate, filtered and concentrated. After a purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v), the desired product **18** was obtained as white crystals (0.140 g; 98 %). Rf: 0.44 (cyclohexane / ethyl

acetate; 50 / 50; v / v); MP: 212 °C; $[\alpha]_D^{20}$: +41.8 (c = 0.5 DCM); IR (ATR): 1743.7; 1373.3; 1282.7; 1222.9; 1128.4; 1091.7; 1035.8; 711.7 cm^{-1}; HRMS: Calcd. for [$C_{37}H_{40}O_{18}NaS$]: m/z 827.1833 $[M+Na]^+$; Found 827.1828 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 – 7.98 (m, 2H, H_{aro}); 7.96 – 7.87 (m, 2H, H_{aro}); 7.60 – 7.48 (m, 2H, H_{aro}); 7.41 (q, *J* = 7.9 Hz, 4H, H_{aro}); 6.55 (d, *J* = 3.7 Hz, 1H, H_1); 5.93 (dd, *J* = 11.3, 9.7 Hz, 1H, H_3); 5.42 (dd, *J* = 9.7, 3.7 Hz, 1H, H_2); 5.31 (t, *J* = 9.2 Hz, 1H, $H_{3'}$); 5.21 (t, *J* = 9.7 Hz, 1H, $H_{4'}$); 5.03 (d, *J* = 10.1 Hz, 1H, $H_{1'}$); 4.92 (dd, *J* = 10.0, 8.9 Hz, 1H, $H_{2'}$); 4.58 (dd, *J* = 12.3, 3.6 Hz, 1H, H_6); 4.55 – 4.44 (m, 2H, H_5, H_6); 4.12 (d, *J* = 9.9 Hz, 1H, $H_{5'}$); 3.73 (s, 3H, -COOC$\underline{H}_3$); 3.36 (t, *J* = 11.2 Hz, 1H, H_4); 2.13 – 1.56 (s, 15H, 5 x C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5 – 168.7 (5 x $CH_3\underline{C}O$-); 166.42 (-$\underline{C}OOCH_3$); 165.9 –165.4 (2 x -O$\underline{C}$OBz); 133.7 – 128.6 (12 C_{aro}); 89.7 (C_1); 81.9 ($C_{1'}$); 75.8 ($C_{5'}$); 73.2 ($C_{3'}$); 71.7 (C_5); 71.6 (C_2) 69.7 ($C_{2'}$), 69.1 ($C_{4'}$); 67.1 (C_3); 63.2 (C_6); 53.1 (-COO$\underline{C}H_3$); 45.8 (C_4); 21.00 – 20.1 (5 x $\underline{C}H_3$CO-).

Synthesis of compounds 19

To a solution of **18** (150 mg; 0.186 mmol) in dry DMF (2 ml), was added pure hydrazine acetate (0.195 mg; 0.212 mmol) under an argon atmosphere. After 1 h of stirring at room temperature, ethyl acetate was added (10 mL) and the mixture was washed with a saturated solution of $NaHCO_3$ (3 x 10 mL) and with a saturated solution of NaCl (10 mL). The organic phase was then dried over sodium sulfate, filtered and evaporated. The desired products **19** was obtained as a mixture of α/β-anomers (90 / 10; NMR ratio) and as white crystals (138.4 mg; 98 %). Rf: 0.30 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 104 °C; $[\alpha]_D^{20}$: +17.6 (c = 0.5 DCM); IR (ATR): 1732.1; 1452.4; 1371.4; 1242.2; 1222.9; 1091.7; 1068.6; 1039.6; 713.7 cm^{-1}; HRMS: Calcd. for [$C_{35}H_{38}O_{17}NaS$]: m/z 785.1727 $[M+Na]^+$; Found 785.1729 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (ddd, *J* = 8.5, 5.1, 1.4 Hz, 4H, H_{aro}); 7.58 – 7.44 (m, 2H, H_{aro}); 7.38 (td, *J* = 7.8, 2.6 Hz, 4H, H_{aro}); 6.04 (dd, *J* = 11.2, 9.7 Hz, 1H, H_3); 5.67 (d, *J* = 3.4 Hz, 1H, H_1); 5.30 (t, *J* = 9.2 Hz, 1H, $H_{3'}$); 5.24 – 5.15 (m, 2H, H_2, $H_{4'}$); 5.04 (d, *J* = 10.1 Hz, 1H, $H_{1'}$); 4.92 (dd, *J* = 10.1, 9.0 Hz, 1H, $H_{2'}$); 4.62 - 4.59 (m, 3H, H_{6a}, $H_{5'}$ H_{6b}); 4.12 (d, *J* = 10.0 Hz, 1H, $H_{5'}$); 3.72 (s, 3H, -COOC$\underline{H}_3$); 3.34 (s, 1H, OH); 3.25 (t, *J* = 10.8 Hz, 1H, H_4); 2.14 – 1.56 (4s, 12H, C$\underline{H}_3$COO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 – 169.5 (4 x $CH_3\underline{C}O$-); 166.7 (-$\underline{C}OOCH_3$); 165.9 – 165.8 (2 x -O$\underline{C}$OBz); 133.6 – 128.6 (12 C_{aro}); 90.7(C_1); 81.5 ($C_{1'}$); 75.5 ($C_{5'}$); 73.6 (C_2); 73.5 ($C_{3'}$), 69.7 ($C_{2'}$); 69.3 ($C_{4'}$); 69.2 (C_5); 67.2 (C_3); 63.5 (C_6); 53.1 (-COO$\underline{C}H_3$); 46.2 (C_4); 21.1 – 20.1 (4 x $\underline{C}H_3$CO-).

Synthesis of compound 20

To a solution of compound **19** (1.281 g; 1.679 mmol) in anhydrous DCM (38 mL), was added trichloroacetonitrile (1.68 mL; 16.79 mmol). The reaction mixture was stirred at room temperature for 15 min. and DBU (0.05 mL; 0.2 eq.; 0.336 mmol) was added at 0 °C. The reaction mixture is then stirred at room temperature under an argon atmosphere for 1 h. The solvent was evaporated and the residue was purified over silica gel chromatography (gradient of cyclohexane / ethyl acetate; 8 / 2; 7 / 3; 6 / 4) to lead to the imidate **20** (1.51 g; 99 %) as white crystals. Rf: 0.35 (cyclohexane / ethyl acetate; 50 / 50; v / v); $[\alpha]_D^{20}$: + 22.6 (c = 0.5 DCM); IR (ATR): 1735.9; 1676.1; 1452.4; 1369.5; 1240.2; 1220.9; 1095.6; 1068.6; 1035.8; 711.7 cm^{-1}; HRMS: Calcd. for [$C_{37}H_{38}NO_{17}NaSCl_3$]: m/z 930.0803 $[M+Na]^+$; Found 930.0801 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H, N$\underline{H}$); 7.95 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 4H, H_{aro}); 7.51 (ddd, *J* = 6.6, 4.6, 3.3 Hz, 2H, H_{aro}); 7.37 (dt, *J* = 11.8, 7.8 Hz, 4H, H_{aro}); 6.78 (d, *J* = 3.5 Hz, 1H, H_1); 6.09 (dd, *J* = 11.4, 9.7 Hz, 1H, H_3); 5.48 (dd, *J* = 9.7, 3.5 Hz, 1H, H_2); 5.31 (t, *J* = 9.3 Hz, 1H, $H_{3'}$); 5.15 (t, *J* = 9.7 Hz, 1H, $H_{4'}$); 5.04 (d, *J* = 10.0 Hz, 1H; $H_{1'}$); 4.92 (dd, *J* = 10.1, 9.0 Hz, 1H, $H_{2'}$); 4.72 – 4.64 (m, 1H, H_{6a}); 4.63 – 4.52 (m, 2H, H_5, H_{6b}); 4.07 – 3.97 (m, 1H, $H_{5'}$); 3.70 (s, 3H, -COOC$\underline{H}_3$); 3.44 – 3.32 (m, 1H, H_4); 2.13 – 1.45 (s, 12H, 4 x C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5 – 169.4 (4 x $CH_3\underline{C}O$-); 166.5 (-$\underline{C}OOCH_3$); 165.6, 165.5 (2 x -O$\underline{C}$OBz); 160.5(-$\underline{C}$=N); 133.7 – 128.6 (12 C_{aro}); 93.8 (C_1); 90.9 (-$\underline{C}Cl_3$); 81.2 ($C_{1'}$); 75.5 ($C_{5'}$); 73.0($C_{3'}$); 72.4 (C_5); 72.1 (C_2); 69.4 ($C_{2'}$); 69.1($C_{4'}$), 66.7 (C_3); 63.1 (C_6); 53.2 (-COO$\underline{C}H_3$); 45.7 (C_4); 21.0 – 19.9 (4 x $\underline{C}H_3$CO-).

Synthesis of compound 21

To a solution of compound **20** (1.469 g; 1.619 mmol) in dry DCM (38 mL) and under an argon atmosphere, was added azidopropan-1-ol (0.48 mL; 5.18 mmol). The reaction mixture was stirred 15 min. at room temperature and then cooled to -15 °C. TMSOTf (0.35 mL; 0.323 mmol) was added and the mixture was gradually warmed up to room temperature. After 2 h of stirring, DMC (40 mL) was added and the mixture was washed with water (30 mL), a saturated solution of $NaHCO_3$ (2 x 30 mL) and water again. The organic phase was dried over sodium sulfate, filtered and concentrated. After purification over silica gel chromatography (cyclohexane / ethyl acetate; 60 / 40; v / v), the desired product **21** was obtained as white crystals (0.977 g; 71.4 %). Rf: 0.47 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 186 °C; $[\alpha]_D^{20}$: - 10.0 (c = 0.5 DCM); IR (ATR): 2098.6; 1745.6; 1373.3; 1244.1; 1093.6; 1068.6; 1035.8; 709, 8 cm^{-1}; HRMS: Calcd. for [$C_{38}H_{43}O_{17}N_3S$]: m/z 868.2211 $[M+Na]^+$; Found 868.2242 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (ddd, *J* = 8.4, 3.7, 1.4 Hz, 4H, H_{aro}); 7.61 – 7.44 (m, 2H, H_{aro}); 7.45 – 7.32 (m, 4H, H_{aro}); 5.62 (dd, *J* = 11.3, 9.4 Hz, 1H, H_3); 5.36 (dd, *J* = 9.4, 7.9 Hz, 1H, H_2); 5.28 (t, *J* = 9.1 Hz, 1H, $H_{3'}$); 5.18 (t, *J* = 9.7 Hz, 1H, $H_{4'}$); 4.98 (d, *J* = 10.0 Hz, 1H, $H_{1'}$); 4.90 (dd, *J* = 10.0, 8.8 Hz, 1H, $H_{2'}$); 4.70 – 4.61 (m, 2H, H_1, H_{6a}); 4.56 (dd, *J* = 12.1, 4.2 Hz, 1H, H_{6b}); 4.13 (d, *J* = 10.0 Hz, 1H, $H_{5'}$); 4.04 – 3.89 (m, 2H, H_5, $H_{1''a}$); 3.75 (s, 3H, -COOC$\underline{H}_3$); 3.58 (ddd, *J* = 9.9, 7.7, 4.8 Hz, 1H,

$H_{1''b}$); 3.35 – 3.07 (m, 3H, $H_{3''a,b}$, H_4); 2.12, 2.03, 1.97.1.53 (4s, 12H, CH_3CO-); 1.77 (ddt, *J* = 13.6, 7.6, 3.1 Hz, 2H, $H_{2''a,b}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 – 169.3 (4 x CH_3CO-); 166.6 (-COOCH_3); 165.8 – 165.3 (-OCOBz); 133.6 – 128.6 (12 C_{aro}); 101.2 (C_1); 81.4 ($C_{1'}$); 75.6 ($C_{5'}$); 74.2(C_5); 73.3(C_2); 73.1 ($C_{3'}$); 70.1(C_3); 69.8($C_{2'}$); 69.1($C_{4'}$); 66.6 ($C_{1''}$); 63.5 (C_6); 53.1 (-COOCH_3); 48.0 ($C_{3''}$); 46.3(C_4); 29.1 ($C_{2''}$); 21.0 – 20.0 (4 x CH_3CO-).

Synthesis of compounds 23, 24, 25 and 26

To a solution of compound **22** (3.817 g; 7.368 mmol) in pyridine (172 mL) was added trityl chloride (10.27 g; 36.84 mmol) and the reaction mixture was stirred at room temperature for 4 days. Then acetic anhydride (60 mL) was added and the reaction was stirred for 3 days. The excess of acetic anhydride was quenched by adding methanol (60 mL) at 0 °C. The reaction mixture was then concentrated under reduced pressure and ethyl acetate was added (50 mL). The organic phase was washed with a saturated solution of $KHSO_4$ (50 mL), with $NaHCO_3$ (75 mL) and with water (75 mL). Then it was dried over sodium sulfate, filtered and evaporated. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 60 / 40; v / v) to afford compounds **23** (9 %), **24** (36 %), **25** (28 %) and **26 (**13 %). Compound **23** analyses: Rf: 0.71 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 96 °C; HRMS: Calcd. for [$C_{90}H_{90}O_{23}Na$]: m/z 1561.5771 [M+Na]$^+$; Found 1561.5729 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 6.94 (m, 45H, (C_6H_5)$_3$C-); 5.49 (d, *J* = 4.2 Hz, 1H, H^{III}_1); 5.37 (t, *J* = 9.9 Hz, 1H, H^{III}_4); 5.29 – 5.20 (m, 1H, H^{I}_3); 5.19 (d, *J* = 4.4 Hz, 1H, H^{II}_1); 5.11 (dt, *J* = 10.0, 8.7 Hz, 2H, H^{II}_3, H^{III}_3); 4.97 – 4.88 (m, 2H, H^{III}_2, H^{I}_2); 4.77 (dd, *J* = 10.3, 4.4 Hz, 1H, H^{II}_2); 4.47 (d, *J* = 7.9 Hz, 1H, H^{I}_1); 4.03 – 3.95 (m, 1H, H^{II}_4); 3.89 (t, *J* = 9.2 Hz, 1H, H^{I}_4); 3.60 (s, 4H, H^{I}_5, -OCH_3); 3.35 (d, *J* = 4.2 Hz, 2H, H^{I}_{6a}, H^{I}_{6b}); 3.30 – 3.25 (m, 1H, H^{III}_5); 3.17 – 3.06 (m, 3H, H^{II}_{6a}, H^{II}_5, H^{III}_{6a}); 2.99 – 2.85 (m, 1H, H^{III}_{6b}); 2.49 – 2.40 (m, 1H, H^{II}_{6b}); 2.11 – 1.66 (m, 21H, CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 – 168.6 (7 x CH_3CO-); 143.7 – 143.5 (9 x Cq C_6H_5); 129.2 – 127.1 (C_{aro}); 101.2 (C^{I}_1); 94.9 (C^{III}_1); 94.8 (C^{II}_1); 86.9 – 86.3 (3 x ((C_6H_5)$_3$C-)); 75.9 (C^{I}_3); 74.3 (C^{I}_5); 73.2 (C^{I}_4); 72.8 (C^{II}_3); 72.6 (C^{I}_2); 70.8 (C^{II}_2); 70.6 (C^{II}_4); 70.5 (C^{III}_3); 70.3 (C^{III}_2); 70.2 (C^{II}_5); 68.9 (C^{III}_5); 67.9 (C^{III}_4); 63.2 (C^{I}_6); 62.5 (C^{III}_6); 60.8 (C^{II}_6); 56.8 (-OCH_3); 21.3 – 20.7 (CH_3CO-). Compound **24** analyses: Rf: 0.6 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 122 °C; $[\alpha]^{20}_D$: +68.2 (c = 0.5 $CHCl_3$); IR (ATR): 1751.36; 1369.46; 1226.73; 1037.70; 765.74; 705, 95 cm^{-1}; HRMS: Calcd. for [$C_{73}H_{78}O_{24}Na$]: m/z 1361.4781 [M+Na]$^+$; Found 1361.4786 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.23 (m, 30H, (C_6H_5)$_3$C-); 5.45 (d, *J* = 4.0 Hz, 1H, H^{III}_1); 5.38 (dd, *J* = 7.5, 2.7 Hz, 2H, H^{III}_3, H^{III}_4); 5.36 – 5.28 (m, 1H); 5.26 – 5.20 (m, 2H, H^{II}_3, H^{I}_3); 5.19 (d, *J* = 4.1 Hz, 1H, H^{II}_1); 5.04 – 4.94 (m, 1H, H^{III}_2); 4.87 (dd, *J* = 9.5, 7.9 Hz, 1H, H^{I}_2); 4.72 (dd, *J* = 10.4, 4.1 Hz, 1H, H^{II}_1); 4.44 (d, *J* = 7.9 Hz, 1H, H^{I}_1); 3.96 – 3.80 (m, 3H, H^{II}_6, H^{I}_4, H^{II}_4); 3.70 (dd, *J* = 12.2, 3.7 Hz, 1H, H^{II}_{6a}); 3.65 (m, 1H, H^{III}_5); 3.61 (s, 3H, OCH_3); 3.56 – 3.45 (m, 3H, H^{I}_{6a}, H^{I}_5, H^{I}_{6b}); 3.43 (dt, *J* = 9.9, 3.1 Hz, 1H, H^{II}_5); 3.22 (dd, *J* = 10.6, 1.8 Hz, 1H, H^{III}_{6a}); 2.90 (dd, *J* = 10.6, 3.0 Hz, 1H, H^{III}_{6b}); 2.13 – 2.01 (s, 24H, 8 x CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 – 169.0 (8 x CH_3CO-) ; 143.8 – 143.5 (6 x Cq C_6H_5); 127.9 – 127.2 (C_{aro}); 101.2 (C^{I}_1); 95.9 (C^{III}_1); 95.5 (C^{II}_1); 87.1 – 86.5 ((C_6H_5)$_3$C); 75.7(C^{I}_3); 74.4 (C^{I}_4); 74.2 (C^{I}_5); 72.5 (C^{I}_2); 72.1(C^{II}_3); 71.9 (C^{II}_4); 70.6 (C^{II}_2); 70.4 (C^{III}_2); 70.3 (C^{III}_4); 69.8 (C^{III}_5); 68.6 (C^{II}_5); 68.3 (C^{III}_3); 63.9 (C^{I}_6); 62.5 (C^{II}_6); 60.7 (C^{III}_6); 56.9 (OCH_3); 21.2 – 20.6 (8 x CH_3CO-). Compound **25** analyses: Rf: 0.47 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 127 °C; $[\alpha]^{20}_D$: +67.6 (c = 0.5 $CHCl_3$); IR (ATR): 1753.29; 1369.46; 1226.73; 1037.70; 765.74; 704, 02 cm^{-1}; HRMS: Calcd. for [$C_{73}H_{78}O_{24}Na$]: m/z 1361.4781 [M+Na]$^+$; Found 1361.4775 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 6.99 (m, 30H, (C_6H_5)$_3$C); 5.46 – 5.35 (m, 2H, H^{III}_1, H^{III}_4); 5.33 – 5.24 (m, 3H, H^{II}_3, H^{II}_1, H^{I}_3); 5.02 (dd, *J* = 10.5, 9.5 Hz, 1H, H^{III}_3); 4.92 – 4.85 (m, 2H, H^{III}_2, H^{II}_2); 4.83 (dd, *J* = 6.4, 4.0 Hz, 1H, H^{I}_2); 4.48 – 4.41 (m, 2H, H^{I}_{6a}, H^{I}_1); 4.28 (dd, *J* = 12.2, 3.8 Hz, 1H, H^{I}_{6b}); 4.16 – 4.05 (m, 1H, H^{II}_4); 4.02 – 3.97 (m, 1H, H^{II}_5); 3.94 (t, *J* = 9.2 Hz, 1H, H^{I}_4); 3.67 (dt, *J* = 9.6, 3.5 Hz, 1H, H^{I}_5); 3.51 (dd, *J* = 10.6, 2.0 Hz, 1H, H^{II}_{6a}); 3.48 (s, 3H, OCH_3); 3.27 – 3.18 (m, 2H, H^{II}_6, H^{III}_5); 3.12 (dd, *J* = 10.7, 1.9 Hz, 1H, H^{III}_{6a}); 2.43 (dd, *J* = 10.6, 2.6 Hz, 1H, H^{III}_{6b}); 2.09 – 1.65 (8s, 24H, CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 – 168.6 (8 x CH_3CO-) 143.8 – 143.4 (6 x Cq C_6H_5); 128.9 – 127.1 (C_{aro}); 101.3 (C^{I}_1); 95.7 (C^{II}_1); 95.1 (C^{III}_1); 87.0 – 86.3 ((C_6H_5)$_3$C); 75.1 (C^{II}_3); 74.4 (C^{I}_4); 72.6 (C^{III}_4); 72.5 (C^{I}_5); 72.2 (C^{II}_2); 71.5 (C^{II}_4); 71.2 (C^{I}_2); 70.7 (C^{II}_5); 70.4 (C^{III}_2); 70.2 (C^{III}_3); 69.3 (C^{III}_5); 67.7 (C^{I}_3); 63.0 (C^{I}_6); 62.7 (C^{II}_6); 60.9 (C^{III}_6); 57.1 (-OCH_3); 21.23 – 20.65 (8 x CH_3CO-). Compound **26** analyses: Rf: 0.49 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 100 °C; HRMS: Calcd. for [$C_{56}H_{66}O_{25}Na$]: m/z 1161.3791 [M+Na]$^+$; Found 1161.3832 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.19 (m, 15H, (C_6H_5)$_3$C); 5.47 (d, *J* = 4.0 Hz, 1H, H^{III}_1); 5.44 – 5.38 (m, 1H, H^{I}_3); 5.36 – 5.22 (m, 4H, H^{III}_3, H^{III}_4, H^{II}_1, H^{II}_3); 5.01 – 4.90 (m, 1H, H^{III}_2); 4.82 – 4.75 (m, 2H, H^{II}_2, H^{I}_2); 4.49 – 4.37 (m, 3H, H^{I}_{6a}, H^{I}_1,H^{II}_{6a}); 4.29 (dd, *J* = 12.1, 4.0 Hz, 1H, H^{I}_{6b}); 4.15 – 4.03 (m, 1H, H^{II}_{6b}); 4.02 – 3.89 (m, 3H, H^{I}_4, H^{II}_4, H^{II}_5); 3.85 – 3.79 (m, 1H, H^{III}_5); 3.70 (dt, *J* = 9.7, 3.5 Hz, 1H, H^{I}_5); 3.48 (s, 3H, -OCH_3); 3.29 (dd, *J* = 10.6, 1.9 Hz, 1H, H^{III}_{6a}); 2.95 (dd, *J* = 10.6, 3.1 Hz, 1H, H^{III}_{6b}); 2.12– 1.69 (s, 27H, 9 x CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 – 169.0 (9 x CH_3CO-); 143.5 (3 x Cq C_6H_5); 128.9 – 127.2 (C_{aro}); 101.2 (C^{I}_1); 96.0 (C^{III}_1); 95.9 (C^{II}_1); 86.6 ((C_6H_5)$_3$C); 75.5 (C^{II}_3); 73.8 (C^{I}_4); 72.3 (C^{I}_2); 72.2 (C^{II}_4); 72.2 (C^{I}_5); 72.0 (C^{I}_3); 70.6 (C^{II}_2); 70.4 (C^{III}_2); 70.2 (C^{III}_4) 69.9 (C^{III}_5); 69.1 (C^{II}_5); 68.1(C^{III}_3); 63.0 (C^{I}_6); 62.3 (C^{II}_6); 60.7 (C^{III}_6); 57.1 (-OCH_3); 21.2 – 20.6 (9 x CH_3CO-).

General procedure A for deprotection of trityl derivatives:

To a solution of compound **23**, **24**, **25** or **26** (1 equiv) in DCM (1 L of DCM / 9 mmol of starting material), was added iron chloride (III) hexahydrate (2 eq. per trityl). The reaction mixture was stirred at room temperature for 1 h. Then the mixture was diluted in DCM (250 mL of DCM / 9 mmol of starting material) and washed 3 times with the same amount of water. The organic phase was dried over sodium sulfate, filtered and concentrated.

Synthesis of compound 27

Using general procedure **A** with compound **23** (5.53 g; 3.59 mmol), the desired product **27** (1.8 g; 62 %) was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 10 / 90; v / v) as white crystals. Rf: 0.10 (cyclohexane / ethyl acetate; 70 / 30; v / v); MP: 128 °C; $[\alpha]_D^{20}$: +72.2 (c = 0.5 $CHCl_3$); IR (ATR): 3475.73; 1747.51; 1371.39; 1232.51; 1033.85 cm^{-1}; HRMS: Calcd. for [$C_{33}H_{48}O_{23}Na$]: m/z 835.2484 [M+Na]$^+$; Found 835.2473 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 – 5.37 (m, 3H, H^{III}_1, H^{II}_3, H^{III}_3); 5.35 (d, *J* = 4.3 Hz, 1H, H^{II}_1); 5.28 (t, *J* = 9.4 Hz, 1H, H^{I}_3); 4.91 (t, *J* = 9.9 Hz, 1H, H^{III}_4); 4.87 – 4.83 (m, 1H, H^{I}_2); 4.82 (dd, *J* = 6.9, 3.7 Hz, 1H, H^{III}_2); 4.74 (dd, *J* = 10.3, 4.3 Hz, 1H, H^{II}_2); 4.43 (d, *J* = 8.0 Hz, 1H, H^{I}_1); 4.21 (t, *J* = 9.4 Hz, 1H, H^{I}_4); 4.07 (t, *J* = 8 Hz, 1H, H^{II}_4); 3.98 – 3.74 (m, 6H, H^{I}_{6a}, H^{II}_{6a}, H^{I}_{6b}, H^{II}_{6b}, H^{II}_5, H^{III}_5); 3.67 (dd, *J* = 12.3, 2.1 Hz, 1H, H^{III}_{6a}); 3.62 – 3.45 (m, 2H, H^{III}_{6b}, H^{I}_5); 3.5 (m, 3H, -OC$\underline{H}_3$); 2.08 – 1.93 (m, 21H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.8 – 169.9 ($CH_3\underline{C}$O-); 101.6 (C^{I}_1); 95.7 (C^{II}_1); 95.4 (C^{III}_1); 75.6 (C^{I}_3); 74.6 (C^{I}_5); 72.5 (C^{II}_3); 72.4 (C^{I}_2); 71.5 (C^{II}_5); 71.1 (C^{II}_4); 71.0 (C^{III}_5); 71.0 (C^{II}_2); 70.8 (C^{I}_4); 70.4 (C^{III}_2); 69.5 (C^{III}_3); 69.1 (C^{III}_4); 61.3 (C^{III}_6); 60.9 (C^{II}_6); 60.6 (C^{I}_6); 57.4 (O$\underline{C}H_3$) 21.2 – 20.6 (s, 21H, 7 x C$\underline{H}_3$CO-).

Synthesis of compound 28

Using general procedure **A** with compound **24** (1.09 g; 0.817 mmol), the desired product **28** (0.612 g; 88 %) was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 20 / 80; v / v) as white crystals. Rf: 0.30 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 110 °C; $[\alpha]_D^{20}$: + 72.6 (c = 0.5 $CHCl_3$); IR (ATR): 3525.88; 1745.58; 1369.46; 1228.66; 1035.77 cm^{-1}; HRMS: Calcd. for [$C_{35}H_{50}O_{24}Na$]: m/z 877.2590 [M+Na]$^+$; Found 877.2598 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 – 5.33 (m, 3H, H^{III}_3, H^{III}_1, H^{II}_3); 5.32 (d, *J* = 4.1 Hz, 1H, H^{II}_1); 5.27 (t, *J* = 9.4 Hz, 1H, H^{I}_3); 4.96 (t, *J* = 9.8 Hz, 1H, H^{III}_4); 4.84 – 4.75 (m, 2H, H^{III}_2, H^{I}_2); 4.71 (dd, *J* = 10.3, 4.1 Hz, 1H, H^{II}_2); 4.50 – 4.41 (m, 2H, H^{II}_{6a}, H^{I}_1); 4.20 (dd, *J* = 12.3, 3.1 Hz, 1H, H^{II}_{6b}); 4.16 – 4.05 (m, 1H, H^{I}_4); 4.02 – 3.90 (m, 3H, H^{III}_{6a}, H^{II}_5, H^{II}_4); 3.86 (dd, *J* = 12.6, 3.2 Hz, 1H, H^{III}_{6b}); 3.71 (ddd, *J* = 10.2, 3.9, 2.4 Hz, 1H, H^{III}_5); 3.62 (dd, *J* = 12.9, 2.3 Hz, 1H, H^{I}_6); 3.58 – 3.49 (m, 2H, H^{I}_5, H^{I}_6); 3.49 (s, 3H, -OC$\underline{H}_3$); 2.12 – 1.95 (m, 24H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0 – 169.8 (8 x $CH_3\underline{C}$O-); 101.5 (C^{I}_1); 95.8 (C^{III}_1); 95.4 (C^{II}_1); 75.5 (C^{I}_3); 74.50 (C^{I}_5); 72.4 (C^{II}_5, C^{I}_2); 72.1 (C^{II}_3); 71.4 (C^{I}_4); 70.9 (C^{II}_2, C^{III}_5); 70.8 (C^{III}_2); 70.3 (C^{III}_3); 69.1 (C^{III}_4, C^{II}_4); 68.8 (C^{II}_6); 62.9 (C^{III}_6); 61.4 (C^{I}_6); 57.3 (O$\underline{C}H_3$); 21.2 – 20.6 (8s, 24H, C$\underline{H}_3$CO-).

Synthesis of compound 29

Using general procedure **A** with compound **25** (1.01 g; 0.761 mmol), the desired product **29** (0.530 g; 82 %) was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 20 / 80; v / v) as white crystals. Rf: 0.27 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 96 °C; $[\alpha]_D^{20}$: +69.4 (c = 0.5 $CHCl_3$); IR (ATR): 3560.59; 1747.51; 1371.39; 1230.58; 1033.85 cm^{-1}; HRMS: Calcd. for [$C_{35}H_{50}O_{24}Na$]: m/z 877.2590 [M+Na]$^+$; Found 877.2600 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46 – 5.35 (m, 3H, H^{II}_3, H^{III}_1, H^{III}_3); 5.28 (d, *J* = 4.1 Hz, 1H, H^{II}_1); 5.23 (t, *J* = 9.1 Hz, 1H, H^{I}_3); 4.90 (t, *J* = 9.9 Hz, 1H,, H^{III}_4); 4.85 – 4.78 (m, 2H, H^{III}_2, H^{I}_2); 4.77 – 4.72 (m, 1H,, H^{II}_2); 4.51 – 4.40 (m, 2H,, H^{I}_{6a}, H^{I}_1); 4.25 (dd, *J* = 12.1, 4.2 Hz, 1H,, H^{I}_{6b}); 4.18 – 4.05 (m, 1H,, H^{II}_4); 3.96 (t, *J* = 9.2 Hz, 1H, H^{I}_4); 3.91 (dd, *J* = 12.9, 2.5 Hz, 1H, H^{I}_{6a}); 3.86 – 3.73 (m, 3H, H^{III}_5, H^{II}_5, H^{II}_{6b}); 3.75 – 3.62 (m, 2H, H^{I}_5, H^{III}_{6a}); 3.56 (dd, *J* = 12.3, 6.5 Hz, 1H, H^{III}_{6b}); 3.48 (s, 3H, -OC$\underline{H}_3$); 2.14 – 1.94 (m, 24H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7 – 169.8 (8 x -O$\underline{C}$OC$\underline{H}_3$); 101.0 (C^{I}_1); 96.0 (C^{II}_1); 95.6 (C^{III}_1); 75.4 (C^{I}_3); 73.4 (C^{I}_4); 72.2 (C^{I}_2); 72.0 (C^{I}_5, C^{II}_3); 71.2 (C^{II}_5); 71.1 (C^{III}_5); 70.7 (C^{II}_2, C^{I}_4); 70.3 (C^{III}_2); 69.4 (C^{III}_3); 68.9 (C^{III}_4); 63.0 (C^{I}_6); 61.4 (C^{III}_6); 60.3 (C^{II}_6), 57.02 (-O$\underline{C}H_3$); 21.0 – 20.5 ($CH_3\underline{C}$O-).

Synthesis of compound 30

Using general procedure **A** with compound **26** (3.13 g; 2.74 mmol), the desired product **30** (0.530 g; 42 %) was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 30 / 70; v / v) as white crystals. Rf: 0.30 (cyclohexane / ethyl acetate; 30 / 70; v / v); MP: 108 °C; $[\alpha]_D^{20}$: +69.4 (c = 0.5 $CHCl_3$); IR (ATR): 3498.37; 1745.58; 1369.46; 1228.66; 1035.77 cm^{-1}; HRMS: Calcd. for [$C_{37}H_{52}O_{25}Na$]: m/z 919.2695 [M+Na]$^+$; Found 919.2692 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45 – 5.32 (m, 3H, H^{III}_3, H^{I}_1, H^{I}_3); 5.29 – 5.18 (m, 2H, H^{II}_1, H^{II}_3); 4.96 (t, *J* = 9.8 Hz, 1H, H^{III}_4); 4.81 (dd, *J* = 7.2, 3.4 Hz, 1H, H^{III}_2); 4.80 – 4.76 (m, 1H, H^{I}_2); 4.73 (dd, *J* = 10.4, 4.0 Hz, 1H, H^{II}_2); 4.50 – 4.40 (m, 3H, H^{I}_{6a}, H^{II}_{6a}, H^{I}_1); 4.30 (dd, *J* = 12.1, 4.1 Hz, 1H, H^{I}_{6b}); 4.16 (dd, *J* = 12.3, 2.7 Hz, 1H, H^{I}_{6b}); 4.01 – 3.88 (m, 3H, H^{II}_4, H^{II}_5, H^{I}_4); 3.75 – 3.66 (m, 2H, H^{I}_5, H^{II}_5); 3.64 (dd, *J* = 12.8, 2.3 Hz, 1H, H^{III}_{6a}); 3.53 (dd, *J* = 12.9, 3.8 Hz, 1H, H^{III}_{6b}); 3.48 (s, 3H, -OC$\underline{H}_3$); 2.18 – 1.95 (m, 27H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8 – 169.9 (9 x -O$\underline{C}$OC$\underline{H}_3$); 101.2 (C^{I}_1); 95.9 (C^{III}_1); 95.8 (C^{II}_1); 75.5 (C^{II}_3); 73.9 (C^{I}_4); 72.4 (C^{I}_4); 72.3 (C^{I}_2); 72.2 (C^{I}_5); 71.8 (C^{I}_3); 70.9 (C^{III}_5); 70.6 (C^{II}_2); 70.4 (C^{III}_2); 69.0 (C^{II}_5, C^{III}_3); 68.7 (C^{III}_4); 63.1 (C^{I}_6); 62.4 (C^{II}_6); 61.1 (C^{III}_6); 57.1 (-O$\underline{C}H_3$); 21.0 – 20.7 (9 x $CH_3\underline{C}$O-).

Synthesis of compound 31

To a solution of compound **27** (0.889 g; 1.09 mmol) in pyridine (70 mL) was added methanesulfonic anhydride (1.90 g; 10.938 mmol). The reaction mixture was stirred at room temperature for 15 h. Then the excess of anhydride was quenched by methanol (20 mL) at 0 °C and the mixture was concentrated under reduced pressure. The residue was diluted in ethyl acetate (50 mL) and washed with a saturated solution of $KHSO_4$ (3 x 50 mL). The organic phase was dried over sodium sulfate, filtered and evaporated. Butanone was added (50 mL) with sodium iodide (3.28 g; 11.16 mmol) and the reaction mixture was heated at reflux for 15 h. After concentration under reduced pressure, the residue was diluted in DCM (50 mL) and washed with water. The organic phase was then dried over sodium sulfate, filtered and evaporated. The desired product **31** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as white crystals (0.976 g; 79 %). Rf: 0.27 (cyclohexane / ethyl acetate; 30 / 70; v / v); MP: 104 °C; $[\alpha]_D^{20}$: +64.2 (c = 0.5 $CHCl_3$); IR (ATR): 1751.36; 1369.46; 1224.80; 1037.70; 680.87; 601.79; 462.92 cm^{-1}; HRMS: Calcd. for $[C_{33}H_{45}O_{20}NaI_3]$: m/z 1164.9536 $[M+Na]^+$; Found 1164.9532 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$) δ 5.44 (d, *J* = 4.2 Hz, 1H, $H^{III}{}_1$); 5.40 (dd, *J* = 8.7, 1.8 Hz, 1H, $H^{II}{}_3$); 5.37 – 5.32 (m, 2H, $H^{III}{}_3$, $H^{II}{}_1$);5.26 (t, *J* = 9.1 Hz, 1H, $H^{I}{}_3$); 4.91 (t, *J* = 9.6 Hz, 1H, $H^{III}{}_4$); 4.85 (d, *J* = 3.9 Hz, 1H, $H^{III}{}_2$); 4.83 – 4.79 (m, 1H, $H^{I}{}_2$); 4.74 (dd, *J* = 10.5, 4.1 Hz, 1H, $H^{II}{}_2$); 4.50 (d, *J* = 7.9 Hz, 1H, $H^{I}{}_1$); 3.89 (t, *J* = 9.0 Hz, 1H, $H^{I}{}_4$); 3.82 (t, *J* = 9.0 Hz, 1H, $H^{I}{}_4$); 3.78 – 3.62 (m, 3H, $H^{II}{}_{6a}$, $H^{III}{}_5$, $H^{I}{}_{6a}$); 3.58 – 3.43 (m, 6H, $H^{II}{}_{6b}$, $H^{II}{}_5$, $H^{I}{}_{6b}$, $H^{III}{}_{6a}$, -OCH_3); 3.37 (ddd, *J* = 9.4, 6.3, 3.0 Hz, 1H, $H^{I}{}_5$); 3.17 (dd, *J* = 11.1, 6.2 Hz, 1H, $H^{III}{}_{6b}$); 2.10 – 1.95 (m, 21H, C$\underline{H_3}$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6 – 169.5 (7 x -O$\underline{C}$OCH_3) 100.9 ($C^{I}{}_1$); 95.5 ($C^{II}{}_1$) 95.5 ($C^{III}{}_1$); 76.7 ($C^{I}{}_4$); 76.6 ($C^{II}{}_4$); 75.0 ($C^{I}{}_3$); 72.5 ($C^{I}{}_5$); 72.4 ($C^{I}{}_4$); 72.4 ($C^{I}{}_2$); 70.8 ($C^{I}{}_3$); 70.5 ($C^{II}{}_2$); 70.4 ($C^{III}{}_2$); 69.4 ($C^{III}{}_5$); 69.3 ($C^{II}{}_5$); 69.0 ($C^{III}{}_3$); 57.2 (-O$\underline{C}$$H_3$) 21.2 – 20.7 (7 x $CH_3\underline{C}$O-); 8.0 ($C^{II}{}_6$); 6.8 ($C^{I}{}_6$); 4.9 ($C^{III}{}_6$).

Synthesis of compound 32

To a solution of compound **28** (1.792 g; 2.098 mmol) in pyridine (60 mL) was added methanesulfonic anhydride (3.655 g; 20.980 mmol). The reaction mixture was stirred at room temperature for 15 h. Then the excess of anhydride was quenched by methanol (39 mL) at 0 °C and the mixture was concentrated under reduced pressure. The residue was diluted in ethyl acetate (20 mL) and washed with a saturated solution of $KHSO_4$ (3 x 20 mL). The organic phase was dried over sodium sulfate, filtered and evaporated. Butanone was added (106 mL) with sodium iodide (6.29 g; 41.96 mmol) and the reaction mixture was heated at reflux for 15 h. After concentration under reduced pressure, the residue was diluted in DCM (20 mL) and washed with water. The organic phase was then dried over sodium sulfate, filtered and evaporated. The desired product **32** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as white crystals (1.86 g; 83 %). Rf: 0.39 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 94 °C; $[\alpha]_D^{20}$: + 67.6 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1224.80; 1037.70; 680.87; 599.86; 524.64; 464.84 cm^{-1}; HRMS: Calcd. for $[C_{35}H_{52}NO_{22}I_2]$: m/z 1092.1070 $[M+NH_4]^+$; Found 1092.1046 $[M+NH_4]^+$; ^1H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.31 (m, 3H, $H^{III}{}_1$, $H^{II}{}_3$, $H^{III}{}_3$); 5.31 – 5.22 (m, 2H, $H^{II}{}_1$, $H^{I}{}_3$); 4.88 (t, J = 9.6 Hz, 1H, $H^{III}{}_4$); 4.85 – 4.76 (m, 3H, $H^{I}{}_2$, $H^{III}{}_2$, $H^{II}{}_2$); 4.55 (dd, J = 12.2, 2.5 Hz, 1H, $H^{II}{}_{6a}$); 4.50 (d, *J* = 7.8 Hz, 1H, $H^{I}{}_1$); 4.36 (dd, *J* = 12.1, 4.1 Hz, 1H, $H^{II}{}_{6b}$); 4.00 – 3.87 (m, 2H, $H^{II}{}_5$, $H^{II}{}_4$); 3.86 – 3.79 (m, 1H, $H^{I}{}_4$); 3.71 (ddd, *J* = 9.6, 6.5, 2.8 Hz, 1H, $H^{III}{}_5$); 3.67 – 3.60 (m, 1H, $H^{I}{}_{6a}$); 3.53 (s, 3H, -OCH_3); 3.42 – 3.32 (m, 2H, $H^{I}{}_5$, $H^{I}{}_{6b}$); 3.27 (dd, *J* = 11.2, 2.8 Hz, 1H, $H^{III}{}_{6a}$); 3.18 – 3.07 (m, 1H, $H^{III}{}_{6b}$); 2.16 – 2.02 (24H, C$\underline{H_3}$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 1707 –169.5 (8 x -O$\underline{C}$OCH_3); 100.9 ($C^{I}{}_1$); 95.7 ($C^{II}{}_1$); 95.6 ($C^{III}{}_1$); 75.1 ($C^{I}{}_4$); 73.4 ($C^{I}{}_3$); 72.5 ($C^{II}{}_4$); 72.4 ($C^{I}{}_5$); 72.3 ($C^{III}{}_4$); 71.5 ($C^{II}{}_3$); 70.5 ($C^{II}{}_2$); 70.3 ($C^{II}{}_2$); 69.5 ($C^{II}{}_5$); 69.3 ($C^{III}{}_5$); 69.0 ($C^{III}{}_3$); 63.4 ($C^{II}{}_6$); 57.2 (-O$\underline{C}$$H_3$); 21.2 – 20.7 ($CH_3\underline{C}$O-); 6.3 ($C^{I}{}_6$); 4.2 ($C^{III}{}_6$).

Synthesis of compound 33

To a solution of compound **29** (1.22 g; 1.428 mmol) in pyridine (40 mL) was added methanesulfonic anhydride (2.49 g; 14.285 mmol). The reaction mixture was stirred at room temperature for 15 h. Then the excess of anhydride was quenched by methanol (15 mL) at 0 °C and the mixture was concentrated under reduced pressure. The residue was diluted in ethyl acetate (20 mL) and washed with a saturated solution of $KHSO_4$ (3 x 20 mL). The organic phase was dried over sodium sulfate, filtered and evaporated. Butanone was added (72 mL) with sodium iodide (4.28 g; 28.6 mmol) and the reaction mixture was heated at reflux for 15 h. After concentration under reduced pressure, the residue was diluted in DCM (20 mL) and washed with water. The organic phase was then dried over sodium sulfate, filtered and evaporated. The desired product **33** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as white crystals (1.302 g; 85 %). Rf: 0.28 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 100 °C; $[\alpha]_D^{20}$: +54.6 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1224.80; 1037.70; 601.79; 540.07 cm^{-1}; HRMS: Calcd. for $[C_{35}H_{52}O_{22}NI_2]$: m/z 1092.1070 $[M+NH_4]^+$; Found 1092.1030 $[M+NH_4]^+$; ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 – 5.39 (m, 2H, $H^{II}{}_3$, $H^{III}{}_1$); 5.35 (dd, *J* = 10.6, 9.3 Hz, 1H, $H^{III}{}_3$); 5.29 (d, *J* = 4.0 Hz, 1H, $H^{II}{}_1$); 5.24 (t, *J* = 9.1 Hz, 1H, $H^{I}{}_3$); 4.93 (t, *J* = 9.6 Hz, 1H, $H^{III}{}_4$); 4.87 – 4.77 (m, 2H, $H^{III}{}_2$, $H^{I}{}_2$); 4.73 (dd, *J* = 10.4, 4.0 Hz, 1H, $H^{II}{}_2$); 4.49 (dd, *J* = 12.1, 3.2 Hz, 1H, $H^{I}{}_{6a}$); 4.44 (d, *J* = 7.8 Hz, 1H, $H^{I}{}_1$); 4.35 (dd, *J* = 12.1, 4.5 Hz, 1H, $H^{I}{}_{6b}$); 3.97 (t, *J* = 9.2 Hz, 1H, $H^{I}{}_4$); 3.82 (t, *J* = 9.0 Hz, 1H, $H^{II}{}_4$); 3.76 – 3.68 (m, 1H, $H^{I}{}_5$); 3.63 (ddd, *J* = 9.8, 5.2, 3.0 Hz, 1H, $H^{III}{}_5$); 3.61 – 3.49 (m, 2H, $H^{II}{}_5$,

H^{III}_3) ; 3.48 (s, 3H, -OC$\underline{H}_3$); 3.19 (dd, *J* = 11.3, 5.3 Hz, 1H, H^{III}_{6b}); 2.15 - 1.94 (m, 24H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 – 169.4 (8 x -O$\underline{C}$OCH$_3$); 101.2 (C^{I}_1); 95.8 (C^{II}_1); 95.5 (C^{III}_1); 76.4 (C^{II}_4); 75.4 (C^{I}_3); 74.3 (C^{I}_4); 72.5 (C^{III}_4) ; 72.3 (C^{I}_2); 72.2 (C^{I}_5); 71.1 (C^{II}_3); 70.7 (C^{III}_2); 70.3 (C^{II}_2); 69.0 (C^{III}_5, C^{III}_3); 68.7 (C^{II}_5); 63.4 (C^{I}_6); 57.1 (–O$\underline{C}$H$_3$); 27.1 –20.7 (8 x CH$_3\underline{C}$O-); 7.68 (C^{II}_6); 5.16 (C^{III}_6).

Synthesis of compound 34

To a solution of compound **30** (0.5 g; 0.558 mmol) in pyridine (36 mL) was added methanesulfonic anhydride (0.97 g; 5.580 mmol). The reaction mixture was stirred at room temperature for 15 h. Then the excess of anhydride was quenched by methanol (10 mL) at 0 °C and the mixture was concentrated under reduced pressure. The residue was diluted in ethyl acetate (50 mL) and washed with a saturated solution of $KHSO_4$ (3 x 50 mL). The organic phase was dried over sodium sulfate, filtered and evaporated. Butanone was added (54 mL) with sodium iodide (1.67 g; 11.16 mmol) and the reaction mixture was heated at reflux for 15 h. After concentration under reduced pressure, the residue was diluted in DCM (50 mL) and washed with water. The organic phase was then dried over sodium sulfate, filtered and evaporated. The desired product **34** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as white crystals (0.503 g; 90 %). Rf: 0.28 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 96 °C; $[\alpha]^{20}_D$: + 79.2 (c = 0.5 $CHCl_3$); IR (ATR): 1745.58; 1369.46; 1224.80; 1037.70; 601.79 cm^{-1}; HRMS: Calcd. for [$C_{37}H_{51}O_{24}NaI$]: m/z 1029.1713 [M+Na]$^+$; Found 1029.1730 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.38 (m, 2H, H^{III}_1, H^{II}_3); 5.38 – 5.31 (m, 1H, H^{III}_3); 5.27 (d, *J* = 4.0 Hz, 1H, H^{II}_1); 5.25 (t, *J* = 8 Hz, 1H, H^{I}_3); 4.89 (t, *J* = 9.6 Hz, 1H, H^{III}_4); 4.84 – 4.78 (m, 2H, H^{I}_2, H^{II}_2); 4.78 – 4.71 (m, 1H, H^{III}_2); 4.50 – 4.41 (m, 3H, H^{I}_{6a}, H^{II}_{6a}, H^{I}_1); 4.32 (dd, *J* = 12.2, 4.3 Hz, 1H, H^{I}_{6b}); 4.27 (dd, *J* = 12.3, 4.1 Hz, 1H, H^{II}_{6b}); 4.02 – 3.87 (m, 3H, H^{II}_5, H^{I}_4, H^{II}_4); 3.68 (m, 2H, H^{I}_5, H^{III}_5); 3.48 (s, 3H, -OC$\underline{H}_3$); 3.27 (dd, *J* = 11.2, 2.9 Hz, 1H, H^{III}_{6a}); 3.13 (dd, *J* = 11.2, 6.1 Hz, 1H, H^{III}_{6b}); 2.15 - 1.95 (m, 27H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.74 – 169.49 (9 x -O$\underline{C}$OCH$_3$); 101.17 (C^{I}_1); 95.79 (C^{II}_1); 95.54 (C^{III}_1); 75.45 (C^{I}_3); 74.0 (C^{I}_4); 73.21 (C^{II}_4); 72.31 (C^{III}_4); 72.29 (C^{I}_2); 72.18 (C^{I}_5); 71.62 (C^{II}_3); 70.54 (C^{II}_2); 70.44 (C^{III}_2); 69.15 (C^{I}_5); 69.0 (C^{III}_5); 69.0 (C^{III}_3); 63.1 (C^{I}_6); 62.9 (C^{II}_6); 57.11 (–O$\underline{C}$H$_3$); 21.04 – 20.69 (9 x CH$_3\underline{C}$O-); 4.19 (C^{III}_6).

Synthesis of compound 35

First step: To a solution of compound **31** (1.670 g; 1.460 mmol) in dry DMF (80 mL) was added potassium thioacetate (1.170 g; 10.24 mmol) under an argon atmosphere and the reaction mixture was stirred at 50 °C. After 1 h of stirring, the solvent was evaporated under reduced pressure and the residue was diluted in ethyl acetate. The mixture was then washed 2 times with a saturated solution of NaCl and the organic phase was dried over sodium sulfate, filtered and evaporated. The *S*-acetylated intermediate was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as light yellow crystals (1.43 g; 99 %). Rf: 0.27 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 94.5 °C; $[\alpha]^{20}_D$: +96.2 (c = 0.5 $CHCl_3$); IR (ATR): 1753.29; 1693.50; 1369.46; 1238.30; 1134.14; 1037.70 cm^{-1}; HRMS: Calcd. for [$C_{39}H_{54}O_{23}NaS_3$]: m/z 1009.2116 [M+Na]$^+$; Found 1009.2131 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 – 5.27 (m, 3H, H^{II}_3, H^{III}_3, H^{III}_1); 5.25 – 5.14 (m, 2H, H^{II}_1, H^{I}_3); 4.94 (t, *J* = 9.7 Hz, 1H, H^{III}_4); 4.86 – 4.76 (m, 2H, H^{III}_2, H^{I}_2); 4.72 (dd, *J* = 10.3, 4.0 Hz, 1H, H^{II}_2); 4.39 (d, *J* = 7.9 Hz, 1H, H^{I}_1); 4.22 – 4.03 (m, 2H, H^{III}_5, H^{II}_5); 3.77 (t, *J* = 9.2 Hz, 1H, H^{I}_4); 3.71 (t, *J* = 9.2 Hz, 1H, H^{I}_4); 3.65 – 3.51 (m, 3H, H^{II}_{6a}, H^{I}_5, H^{I}_{6a}); 3.48 (s, 3H, -OC$\underline{H}_3$); 3.21 (dd, *J* = 4.3, 2.8 Hz, 2H, $H^{III}_{6a,b}$); 3.13 – 3.07 (m, 1H, H^{I}_{6b}); 3.07 – 3.01 (m, 1H, H^{II}_{6b}); 2.44 – 2.27 (m, 9H, -SCOC$\underline{H}_3$); 2.09 – 1.92 (m, 21H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5 – 194.1 (3 x -S$\underline{C}$OCH$_3$); 170.8 – 169.7 (7 x -$\underline{C}$OCH$_3$) 101.1 (C^{I}_1); 95.8 (C^{III}_1); 95.6 (C^{II}_1); 76.4 (C^{I}_4); 76.1 (C^{II}_4); 75.3 (C^{I}_3); 73.6 (C^{I}_5); 72.4 (C^{I}_2); 71.6 (C^{II}_3); 70.7 (C^{II}_2) 70.3 (C^{III}_2); 70.1 (C^{III}_4); 69.9 (C^{II}_5); 69.7 (C^{III}_3) 69.4 (C^{III}_5); 57.0 (-O$\underline{C}$H$_3$); 31.7 (C^{II}_6); 31.3 (C^{I}_6); 30.8 (-SCO$\underline{C}$H$_3$); 30.6 (2 x -SCO$\underline{C}$H$_3$); 29.9 (C^{III}_6); 21.1 – 20.7 (7 x CH$_3\underline{C}$O-).

Second step: To a solution of the previous *S*-acetylated derivative (1.386 g; 1.405 mmol) in DMA (9.37 mL) and under an argon atmosphere, were added dithiothreitol (1.95 g; 12.65 mmol) and $NaHCO_3$ (23.61 mg; 0.281 mmol). After 6 h of stirring at 40 °C, the reaction is not completed and reactants are added in same proportions. After 10 h, no starting material was observed and toluene (20 mL) was added. The mixture was washed 2 times with a saturated solution of NaCl (20 mL) and the organic phase was dried over sodium sulfate, filtered then evaporated under reduced pressure. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired compound **35** (0.64 g; 55 %) as white crystals. Rf: 0.54 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 104 °C; $[\alpha]^{20}_D$: +91.2 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1240.23; 1041.56 cm^{-1}; HRMS: Calcd. for [$C_{31}H_{46}O_{19}NaS_3$]: m/z 841.1693 [M+Na]$^+$; Found 841.1786 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 – 5.33 (m, 2H, H^{II}_3, H^{III}_1); 5.33 – 5.28 (m, 1H, H^{II}_1); 5.25 (t, *J* = 9.2 Hz, 1H, H^{I}_3); 5.20 – 5.11 (m, 1H, H^{III}_3); 4.85 – 4.76 (m, 2H, H^{I}_2, H^{III}_2); 4.72 (dd, *J* = 10.4, 4.1 Hz, 1H, H^{II}_2); 4.46 (d, *J* = 7.9 Hz, 1H, H^{I}_1); 3.99 (m, 2H, H^{I}_4, H^{II}_4); 3.87 (ddd, *J* = 9.2, 5.7, 2.9 Hz, 1H, H^{II}_5); 3.76 – 3.68 (m, 2H, H^{III}_4, H^{III}_5); 3.62 (ddd, *J* = 9.6, 6.8, 2.9 Hz, 1H, H^{I}_5); 3.52 (s, 3H); 3.13 – 2.97 (m, 3H, H^{II}_{6a}, H^{I}_{6a}, H^{III}_{6a}); 2.96 – 2.74 (m, 3H, H^{I}_{6b}, H^{II}_{6b}, H^{III}_{6b}); 2.13 – 1.93 (m, 18H, C$\underline{H}_3$CO-); 1.83 (t, *J* = 8.3 Hz, 1H, -SH ^{I}); 1.72 (t, *J* = 8.4 Hz, 1H, -SH ^{II}); 1.61 (t, *J* = 8.6 Hz, 1H, -SH ^{III}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0 – 169.9 (6 x -$\underline{C}$OCH$_3$); 101.2 (C^{I}_1);

95.6 (C^{III}_1); 95.5 (C^{II}_1); 75.5 (C^{I}_3); 74.7 (C^{I}_4); 74.3 (C^{I}_5); 73.6 (C^{II}_4); 72.8 (C^{III}_3); 72.7 (C^{III}_4); 72.5 (C^{I}_2); 72.0 (C^{II}_3); 70.9 (C^{III}_5); 70.8 (C^{II}_5); 70.7 (C^{I}_2); 70.0 (C^{III}_2); 57.2 (-O<u>C</u>H$_3$); 27.4 (C^{I}_6); 27.0 (C^{II}_6); 26.2 (C^{III}_6); 21.1 – 20.7 (6 x CH$_3$<u>C</u>O-).

Synthesis of compound 36

First step: To a solution of compound **32** (1.220 g; 1.135 mmol) in dry DMF (56 mL) was added potassium thioacetate (0.518 g; 4.540 mmol) under an argon atmosphere and the reaction mixture was stirred at 50 °C. After 1 h of stirring, the solvent was evaporated under reduced pressure and the residue was diluted in ethyl acetate. The mixture was then washed 2 times with a saturated solution of NaCl and the organic phase was dried over sodium sulfate, filtered and evaporated. The desired *S*-acetylated intermediate was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as light yellow crystals (1.09 g; 99 %). Rf: 0.46 (cyclohexane / ethyl acetate; 60 / 40; v / v); MP: 91 °C; $[\alpha]_D^{20}$: +49.8 (c = 0.5 $CHCl_3$); IR (ATR): 1749.44; 1695.43; 1369.46; 1224.80; 1136.07; 1037.70 cm^{-1}; HRMS: Calcd. for [$C_{39}H_{54}O_{25}NaS_2$]: m/z 988.2790 [M+Na]$^+$; Found 988.2803 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (dd, *J* = 10.3, 8.8 Hz, 1H, H^{II}_3); 5.37 – 5.28 (m, 2H, H^{III}_1, H^{III}_3); 5.27 – 5.16 (m, 2H, H^{II}_1, H^{I}_3); 4.92 (t, *J* = 9.6 Hz, 1H, H^{III}_4); 4.84 – 4.73 (m, 3H, H^{III}_2, H^{I}_2, H^{II}_2); 4.48 – 4.36 (m, 2H, H^{II}_{6a}, H^{I}_1); 4.30 (dd, *J* = 12.2, 4.4 Hz, 1H, H^{II}_{6b}); 4.17 (ddd, *J* = 9.8, 4.4, 2.7 Hz, 1H, H^{II}_5); 4.03 (ddd, *J* = 10.0, 5.0, 3.3 Hz, 1H, H^{III}_5); 3.89 (t, *J* = 9.4 Hz, 1H, H^{II}_4); 3.76 (dd, *J* = 10.0, 7.9 Hz, 1H, H^{I}_4); 3.72 – 3.64 (m, 1H, H^{I}_{6a}); 3.60 (ddd, *J* = 9.5, 8.0, 3.0 Hz, 1H, H^{I}_5); 3.48 (d, *J* = 8.4 Hz, 3H, -OC<u>H</u>$_3$); 3.15 (qd, *J* = 14.5, 4.2 Hz, 2H, H^{III}_{6a}, H^{III}_{6b}); 2.97 (dd, *J* = 13.7, 8.0 Hz, 1H, H^{I}_{6b}); 2.37 (S, 3H, -SCOC<u>H</u>$_3$); 2.33 (s, 3H, -SCOC<u>H</u>$_3$); 2.14 – 1.90 (m, 24H, C<u>H</u>$_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.4 – 194.2 (2 x -S<u>C</u>OCH$_3$); 170.8 –169.7 (8 x -<u>C</u>OCH$_3$); 101.0 (C^{I}_1); 96.1 (C^{II}_1); 95.6 (C^{III}_1); 76.8 (C^{I}_4); 75.4 (C^{I}_3); 73.4 (C^{I}_5); 73.3 (C^{II}_4); 72.4 (C^{II}_2); 71.7 (C^{II}_3); 70.5 (C^{I}_2); 70.2 (C^{III}_2); 70.1 (C^{III}_4); 69.5 (C^{III}_3); 69.4 (C^{III}_5); 69.3 (C^{II}_5); 63.0 (C^{II}_6); 57.0 (-O<u>C</u>H$_3$); 31.5 (C^{I}_6); 30.6 (2 x -SCO<u>C</u>H$_3$); 29.7 (C^{III}_6); 21.1 – 20.7 (8 x CH$_3$<u>C</u>O-).

Second step: To a solution of the previous *S*-acetylated derivative (1.15 g; 1.185 mmol) in DMA (7.9 mL) and under an argon atmosphere, were added dithiothreitol (1.09 g; 7.11 mmol) and $NaHCO_3$ (19.91 mg; 0.237 mmol). After 6 h of stirring at 40 °C, the reaction is not completed and reactants are added in same proportions. After 10 h, no starting material was observed and toluene (20 mL) was added. The mixture was washed 2 times with a saturated solution of NaCl (20 mL) and the organic phase was dried over sodium sulfate, filtered then evaporated under reduced pressure. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired compound **36** (0.848 g; 87 %) obtained as white crystals. Rf: 0.38 (cyclohexane / ethyl acetate; 40 / 60; v / v); MP: 90 °C; $[\alpha]_D^{20}$: +81.4 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1228.66; 1037.70 cm^{-1}; HRMS: Calcd. for [$C_{35}H_{54}NO_{22}S_2$]: m/z 904.2579 [M+NH_4]$^+$; Found 904.2620 [M+NH_4]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 – 5.31 (m, 3H, H^{III}_1, H^{III}_3, H^{II}_3); 5.29 – 5.19 (m, 2H, H^{II}_1, H^{I}_3); 5.03 (t, *J* = 9.6 Hz, 1H, H^{III}_4); 4.85 – 4.69 (m, 3H, H^{III}_2, H^{I}_2, H^{II}_2); 4.52 – 4.41 (m, 2H, H^{II}_{6a}, H^{I}_1); 4.26 (dd, *J* = 12.1, 4.1 Hz, 1H, H^{II}_{6b}); 4.00 (t, *J* = 9.1 Hz, 1H, H^{I}_4); 3.96 – 3.80 (m, 3H, H^{II}_5, H^{II}_4, H^{III}_5); 3.63 (ddd, *J* = 9.3, 6.4, 2.9 Hz, 1H, H^{I}_5); 3.51 (s, 3H, -OC<u>H</u>$_3$); 3.16 – 3.00 (m, 1H, H^{I}_{6a}); 2.81 (ddd, *J* = 14.3, 8.2, 6.4 Hz, 1H, H^{I}_{6b}); 2.67 (ddd, *J* = 14.4, 9.0, 3.1 Hz, 1H, H^{III}_{6a}); 2.57 (ddd, *J* = 14.4, 8.3, 6.1 Hz, 1H, H^{III}_{6b}); 2.15 – 1.93 (m, 24H, CH$_3$CO-); 1.81 (t, *J* = 8.3 Hz, 1H, -SH^{I}); 1.69 (t, *J* = 8.6 Hz, 1H, -SH^{III}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7 – 169.7 (8 x -<u>C</u>OCH$_3$); 101.1 (C^{I}_1); 95.8 (C^{II}_1); 95.5 (C^{III}_1); 75.5 (C^{I}_3); 75.2 (C^{I}_4); 73.9 (C^{I}_5);72.8 (C^{II}_5); 72.4 (C^{I}_2); 71.9 (C^{II}_3); 70.5 (C^{III}_4); 70.4 (C^{II}_2, C^{III}_5); 70.3 (C^{III}_2); 69.3 (C^{III}_3); 69.2 (C^{II}_4); 63.4 (C^{I}_6); 57.2 (-O<u>C</u>H$_3$); 27.0 (C^{I}_6); 26.0 (C^{III}_6); 21.2 – 20.7 (8 x CH$_3$<u>C</u>O-).

Synthesis of compound 37

First step: To a solution of compound **33** (2.540 g; 2.364 mmol) in dry DMF (117 mL) was added potassium thioacetate (1.35 g; 11.82 mmol) under an argon atmosphere and the reaction mixture was stirred at 50 °C. After 1 h of stirring, the solvent was evaporated under reduced pressure and the residue was diluted in ethyl acetate. The mixture was then washed 2 times with a saturated solution of NaCl and the organic phase was dried over sodium sulfate, filtered and evaporated. The desired *S*-acetylated intermediate was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as light yellow crystals (2.20 g; 96 %). Rf: 0.23 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 88 °C; $[\alpha]_D^{20}$: +61.8 (c = 0.5 $CHCl_3$); IR (ATR): 1751.36; 1695.43; 1369.46; 1226.73; 1132.21; 1037.70 cm^{-1}; HRMS: Calcd. for [$C_{39}H_{58}NO_{24}S_2$]: m/z 988.2790 [M+NH_4]$^+$; Found 988.2805 [M+NH_4]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.30 (m, 3H, H^{II}_3, H^{III}_3, H^{III}_1); 5.29 – 5.21 (m, 2H, H^{II}_1, H^{I}_3); 4.96 (t, J = 9.7 Hz, 1H, H^{III}_4); 4.88 – 4.74 (m, 2H, H^{III}_2, H^{I}_2); 4.70 (dd, J = 10.3, 4.0 Hz, 1H, H^{II}_2); 4.51 – 4.36 (m, 3H, H^{I}_{6a}, H^{I}_1, H^{I}_{6b}); 4.20 – 4.08 (m, 1H, H^{III}_5); 3.98 – 3.89 (m, 2H, H^{II}_5, H^{I}_4); 3.77 – 3.62 (m, 2H, H^{II}_4, H^{I}_5); 3.53 (dd, J = 13.9, 3.1 Hz, 1H, H^{II}_{6a}); 3.50 (s, 3H, -OC<u>H</u>$_3$); 3.26 – 3.17 (m, 2H, H^{III}_{6a}, H^{III}_{6b}); 3.02 (dd, J = 13.8, 7.8 Hz, 1H, H^{II}_{6b}); 2.41 (s, 3H,-SCOC<u>H</u>$_3$); 2.34 (s, 3H, -SCOC<u>H</u>$_3$); 2.19 (s, 3H, CH$_3$<u>C</u>O-); 2.09 – 1.99 (m, 21H, C<u>H</u>$_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4 – 193.9 (2 x -S<u>C</u>OCH$_3$); 170.8 –169.8 (8 x -<u>C</u>OCH$_3$); 101.2 (C^{I}_1); 95.9 (C^{III}_1); 95.5 (C^{II}_1); 75.8 (C^{II}_4); 75.3 (C^{I}_3); 74.3 (C^{I}_4); 72.2 (C^{I}_2, C^{I}_5); 72.2 (C^{III}_3); 71.7 (C^{II}_2); 70.8 (C^{II}_2); 70.2 (C^{III}_2); 70.0 (C^{III}_4); 69.8 (C^{II}_5); 69.6 (C^{III}_5); 69.5 (C^{II}_3); 63.4 (C^{I}_6); 57.1 (-O<u>C</u>H$_3$); 31.2 (C^{II}_6); 30.7 (-SCO<u>C</u>H$_3$); 30.5 (-SCO<u>C</u>H$_3$); 29.9 (C^{III}_6); 21.1 – 20.7 (8 x C<u>H</u>$_3$CO-).

Second step: To a solution of the previous *S*-acetylated derivative (2.19 g; 2.257 mmol) in DMA (15 mL) and under an argon atmosphere, were added dithiothreitol (2.09 g; 13.55 mmol) and $NaHCO_3$ (37.93 mg; 0.451 mmol). After 20 h of stirring at 40 °C, no starting material was observed and toluene (20 mL) was added. The mixture was washed 2 times with a saturated solution of NaCl (20 mL) and the organic phase was dried over sodium sulfate, filtered then evaporated under reduced pressure. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired product **37** (1.40 g; 70 %) as with crystals. Rf: 0.39 (cyclohexane / ethyl acetate; 40 / 60; v / v); MP: 208 °C; $[\alpha]_D^{20}$: +84.2 (c = 0.5 $CHCl_3$); IR (ATR): 1751.36; 1371.39; 1240.23; 1224.80; 1031.92 cm^{-1}; HRMS: Calcd. for [$C_{35}H_{54}NO_{22}S_2$]: m/z 904.2579 $[M+NH_4]^+$; Found 904.2594 $[M+NH_4]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.28 (m, 3H, H^{III}_3, H^{III}_1, H^{II}_3); 5.28 – 5.16 (m, 2H, H^{II}_1, H^{I}_3); 5.04 (t, *J* = 9.7 Hz, 1H, H^{III}_4); 4.85 – 4.75 (m, 2H, H^{III}_2, H^{I}_2); 4.68 (dd, *J* = 10.3, 3.5 Hz, 1H, H^{II}_2); 4.49 (dd, *J* = 12.0, 3.3 Hz, 1H, H^{I}_{6a}); 4.42 (dd, *J* = 7.8, 1.7 Hz, 1H, H^{I}_1); 4.34 (dd, *J* = 12.0, 4.5 Hz, 1H, H^{I}_{6b}); 4.00 – 3.90 (m, 3H, H^{II}_4, H^{II}_5, H^{I}_4); 3.84 (ddd, *J* = 9.4, 5.8, 3.1 Hz, 1H, H^{III}_5); 3.75 – 3.64 (m, 1H, H^{I}_5); 3.47 (s, 3H, -OC$\underline{H}_3$); 2.98 (ddd, *J* = 14.0, 8.0, 2.2 Hz, 1H, H^{II}_{6b}); 2.87 – 2.68 (m, 1H, H^{II}_{6b}, H^{III}_{6a}); 2.58 (ddd, *J* = 14.3, 8.3, 5.8 Hz, 1H, H^{III}_{6b}); 2.13 – 1.95 (8s, 24H, C$\underline{H}_3$CO-); 1.74 (t, *J* = 8.3 Hz, 1H, -SH ^{II}); 1.70 (t, *J* = 8.6 Hz, 1H, -SH ^{III}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 – 169.6 (8 x -C$\underline{O}$C$\underline{H}_3$); 101.0 (C^{I}_1); 95.5 (C^{II}_1); 95.4 (C^{III}_1); 75.3 (C^{I}_3); 73.9 (C^{I}_4); 73.6 (C^{II}_4); 72.1(C^{III}_1); 72.1 (C^{I}_2, C^{I}_5); 71.6 (C^{III}_3); 70.8 (C^{II}_2); 70.3 (C^{III}_1); 70.3 – 70.2 (C^{III}_4, C^{III}_2, C^{II}_5, C^{III}_5); 69.2 (C^{II}_3); 63.3 (C^{I}_6); 57.0 (-O$\underline{C}$H$_3$); 26.8 (C^{II}_6); 25.9 (C^{III}_6); 21.0 –20.6 (8 x C$H_3\underline{C}$O-).

Synthesis of compound 38

First step: To a solution of compound **34** (1.018 g; 1.011 mmol) in dry DMF (46 mL) was added potassium thioacetate (0.577 g; 5.056 mmol) under an argon atmosphere and the reaction mixture was stirred at 50 °C. After 1 h of stirring, the solvent was evaporated under reduced pressure and the residue was diluted in ethyl acetate. The mixture was then washed 2 times with a saturated solution of NaCl and the organic phase was dried over sodium sulfate, filtered and evaporated. The desired *S*-acetylated intermediate was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) as light yellow crystals (0.88 g; 92 %). Rf: 0.21 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 91 °C; $[\alpha]_D^{20}$: +71.6 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1699.29; 1369.46; 1226.73; 1134.14; 1037.70 cm-1; HRMS: Calcd. for [$C_{39}H_{54}O_{25}NaS$]: m/z 977.2573 $[M+Na]^+$; Found 977.2620 $[M+Na]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (dd, *J* = 10.4, 8.8 Hz, 1H, H^{II}_3); 5.34 – 5.29 (m, 2H, H^{III}_3, H^{III}_1); 5.28 – 5.20 (m, 2H, H^{I}_3, H^{II}_1); 4.91 (t, *J* = 9.7 Hz, 1H, H^{III}_4); 4.82 – 4.76 (m, 2H, H^{I}_2, H^{III}_2); 4.73 (dd, *J* = 10.3, 4.1 Hz, 1H, H^{II}_2); 4.49 – 4.42 (m, 2H, H^{I}_{6a}, H^{I}_1); 4.38 (dd, *J* = 12.2, 2.8 Hz, 1H, H^{II}_{6a}); 4.33 (dd, *J* = 12.1, 4.2 Hz, 1H, H^{I}_{6b}); 4.21 (dd, *J* = 12.2, 4.1 Hz, 1H, H^{II}_{6b}); 4.01 – 3.91 (m, 3H, H^{II}_5, H^{I}_4, H^{III}_5); 3.88 (dd, *J* = 9.8, 8.8 Hz, 1H, H^{II}_4); 3.75 – 3.64 (m, 1H, H^{I}_5); 3.48 (s, 3H, -OC$\underline{H}_3$); 3.18 – 3.06 (m, 2H, $H^{III}_{6a,b}$); 2.34 (s, 3H, -SCOC$\underline{H}_3$); 2.20 – 1.91 (m, 27H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3 (-S$\underline{C}$OCH$_3$); 170.7 – 169.8 (9 x -$\underline{C}$OCH$_3$); 101.2 (C^{I}_1); 95.8 (C^{II}_1); 95.6 (C^{III}_1); 75.4 (C^{I}_3); 74.0 (C^{I}_4) 73.0 (C^{II}_4); 72.3 (C^{I}_2); 72.2 (C^{I}_5); 71.8 (C^{II}_3); 70.6(C^{II}_2) 70.3 (C^{III}_2); 70.1 (C^{III}_4); 69.6 (C^{III}_5) 69.4 (C^{III}_3); 69.1 (C^{II}_5); 63.1 (C^{I}_6); 62.8 (C^{II}_6); 57.1 (-O$\underline{C}$H$_3$); 30.6 (-SCO$\underline{C}$H$_3$); 29.8 (C^{III}_6); 21.2 – 20.7 (C$\underline{H}_3$CO-).

Second step: To a solution of the previous *S*-acetylated derivative (0.770 g; 0.806 mmol) in DMA (5.4 mL) and under an argon atmosphere, were added dithiothreitol (0.372 g; 2.419 mmol) and $NaHCO_3$ (13.54 mg; 0.161 mmol). After 20 h of stirring at 40 °C, no starting material was observed and toluene (20 mL) was added. The mixture was washed 2 times with a saturated solution of NaCl (20 mL) and the organic phase was dried over sodium sulfate, filtered then evaporated under reduced pressure. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired product **38** (0.555 g; 75 %) as with crystals. Rf: 0.31 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 93 °C; $[\alpha]_D^{20}$: +83.2 (c = 0.5 $CHCl_3$); IR (ATR): 1745.58; 1369.46; 1226.73; 1037.70 cm^{-1}; HRMS: Calcd. for [$C_{37}H_{52}O_{24}NaS$]: m/z 935.2483 $[M+Na]^+$; Found 935.2484 $[M+Na]^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 – 5.30 (m, 3H, H^{II}_3, H^{III}_1, H^{III}_3); 5.29 – 5.19 (m, 2H, H^{I}_3, H^{II}_1); 5.04 (t, *J* = 9.7 Hz, 1H, H^{III}_4); 4.83 – 4.76 (m, 2H, H^{I}_2, H^{III}_2); 4.74 (dd, *J* = 10.4, 4.1 Hz, 1H, H^{II}_2); 4.51 – 4.40 (m, 3H, H^{I}_{6a}, H^{I}_1, H^{II}_{6a}); 4.33 (dd, *J* = 12.1, 4.2 Hz, 1H, H^{I}_{6b}); 4.22 (dd, *J* = 12.2, 4.0 Hz, 1H, H^{II}_{6b}); 4.04 – 3.90 (m, 3H, H^{II}_5, H^{I}_4, H^{II}_4); 3.86 (ddd, *J* = 9.4, 5.8, 3.0 Hz, 1H, H^{III}_5); 3.71 (ddd, *J* = 9.6, 4.2, 3.1 Hz, 1H, H^{I}_5); 3.47 (s, 3H, -OC$\underline{H}_3$); 2.67 (ddd, *J* = 14.4, 9.0, 3.1 Hz, 1H, H^{III}_{6a}); 2.56 (ddd, *J* = 14.3, 8.3, 5.9 Hz, 1H, H^{III}_{6b}); 2.15 – 1.90 (m, 27H, C$\underline{H}_3$CO-); 1.68 (t, *J* = 8.6 Hz, 1H, -SH ^{III}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 – 169.9 (9 x -$\underline{C}$OCH$_3$); 101.3 (C^{I}_1); 96.0 (C^{II}_1); 95.7 (C^{III}_1); 75.6 (C^{I}_3); 74.2 (C^{I}_4); 72.9 (C^{II}_4); 72.4 (C^{III}_2); 72.3 (C^{I}_5); 72.0 (C^{II}_3); 70.7 (C^{I}_2); 70.6 (C^{II}_2); 70.6 (C^{III}_4); 70.4 (C^{III}_5); 69.4 (C^{III}_3); 69.2 (C^{II}_5); 63.3 (C^{I}_6); 63.1 (C^{II}_6); 57.3 (-O$\underline{C}$H$_3$); 26.1 (C^{III}_6); 21.3 – 20.8 (CH$_3\underline{C}$O-).

Synthesis of compound 39

To a solution of compound **35** (448 mg; 0.547 mmol) in anhydrous DMF (20 mL) were added triethylamine (0.37 mL; 2.738 mmol) and dithiothreitol (164 mg; 1.095 mmol) under an argon atmosphere. The mixture was stirred for a few minutes at room temperature and propargyl bromide was added dropwise (80 % in toluene; 0.405 mL; 3.833 mmol). After 6 h, reactants (Et3N, DTT and Propargyl bromide) were added in the same proportions. After 3 h of stirring, the reaction mixture was evaporated and diluted in toluene (30 mL). Then it was washed several times with

a saturated solution of NaCl (30 mL) and finally with water. The organic phases were combined and dried over sodium sulfate, filtered and concentrated. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired product **39** as white crystals (394 mg; 77 %). Rf: 0.31 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 74 °C; $[\alpha]_D^{20}$: +126.0 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1238.30; 1037.70; 700.16 cm^{-1}; HRMS: Calcd. for $[C_{40}H_{52}O_{19}NaS_3]$: m/z 955.2163 $[M+Na]^+$; Found 955.2188 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 5.41 (dd, *J* = 10.5, 9.0 Hz, 1H, H^{II}_3); 5.35 (d, *J* = 4.1 Hz, 1H, H^{III}_1); 5.31 (d, *J* = 4.1 Hz, 1H, H^{II}_1); 5.24 (t, *J* = 9.2 Hz, 1H, H^{I}_3); 5.14 (dd, *J* = 10.6, 9.3 Hz, 1H, H^{III}_3); 4.86 – 4.75 (m, 2H, H^{I}_2, H^{III}_2); 4.72 (dd, *J* = 10.5, 4.1 Hz, 1H, H^{II}_2); 4.43 (d, *J* = 7.9 Hz, 1H, H^{I}_1); 4.21 – 4.07 (m, 1H, H^{II}_5); 3.97 (ddd, *J* = 9.3, 6.1, 3.0 Hz, 1H, H^{III}_5); 3.94 – 3.85 (m, 2H, H^{I}_4, H^{II}_4); 3.77 – 3.60 (m, 2H, H^{I}_5, H^{III}_4); 3.50 (s, 3H, -OC$\underline{H}_3$); 3.47 – 3.16 (m, 9H, H^{I}_{6a}, -C$\underline{H}_2$S- Propargyl I, II, III, H^{II}_{6a}, H^{III}_{6a}); 3.07 – 2.91 (m, 3H, H^{II}_{6b}, H^{I}_{6b}, H^{III}_{6b}); 2.62 (t, *J* = 2.5 Hz, 1H, -C$\underline{H}$ Propargyl I); 2.43 (t, *J* = 2.5 Hz, 1H, -C$\underline{H}$ Propargyl II); 2.29 (t, *J* = 2.6 Hz, 1H, -C$\underline{H}$ Propargyl III); 2.15 – 1.91 (m, 18H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.5 – 169.8 (6 x -$\underline{C}$OC$\underline{H}_3$); 101.1 (C^{I}_1); 95.2 (C^{II}_1); 95.2 (C^{III}_1); 80.2 (Cq III); 79.9 (Cq II); 79.7 (Cq I); 75.5 (C^{I}_3); 75.3 (C^{I}_4); 74.1 (C^{II}_4); 74.0 (C^{I}_5); 73.1 (C^{III}_5); 72.9 (-$\underline{C}$H Propargyl I); 72.4 (C^{I}_2); 72.3 (-$\underline{C}$H Propargyl II); 72.2 (C^{III}_3); 71.9 (C^{II}_3); 71.4 (-$\underline{C}$H Propargyl III); 71.4 (C^{III}_4); 71.3 (C^{II}_5); 70.6 (C^{II}_2); 70.0 (C^{III}_2); 56.9 (-O$\underline{C}$H$_3$); 33.5 (C^{I}_6); 33.0 (C^{II}_6); 21.0 (C^{III}_6); 20.89 (-CH_2- Propargyl III); 20.82 (-CH_2- Propargyl II); 20.2 (-CH_2- Propargyl I); 20.9 – 20.5 (6 x $CH_3\underline{C}$O-).

Synthesis of compound 40

To a solution of compound **36** (0.486 g; 0.547 mmol) in anhydrous DMF (20 mL) were added triethylamine (0.304 mL; 1.136 mmol) and dithiothreitol (0.169 g; 0.568 mmol) under an argon atmosphere. The mixture was stirred for a few minutes at room temperature and propargyl bromide was added dropwise (80 % in toluene; 0.295 mL; 2.739 mmol). After 6 h, reactants (Et3N, DTT and Propargyl bromide) were added in the same proportions. After 3 h of stirring, the reaction mixture was evaporated and diluted in toluene (30 mL). Then it was washed several times with a saturated solution of NaCl (30 mL) and finally with water. The organic phases were combined and dried over sodium sulfate, filtered and concentrated. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired product **40** as white crystals (0.39 g; 74 %). Rf: 0.38 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 71 °C; $[\alpha]_D^{20}$: + 125.6 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1226.73; 1037.70; 702.09 cm^{-1}; HRMS: Calcd. for $[C_{41}H_{54}O_{22}S_2Na]$: m/z 985.2446 $[M+Na]^+$; Found 985.2434 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 5.41 (dd, J = 10.4, 9.0 Hz, 1H, H^{II}_3); 5.37 (d, J = 3.9 Hz, 1H, H^{III}_1); 5.34 – 5.20 (m, 3H, H^{I}_1, H^{III}_3, H^{I}_3); 5.01 (t, J = 9.7 Hz, 1H, H^{III}_4); 4.82 – 4.68 (m, 3H, H^{I}_2, H^{III}_2, H^{I}_2); 4.47 (dd, J = 12.1, 3.0 Hz, 1H, H^{II}_{6a}); 4.42 (d, J = 8.0 Hz, 1H, H^{I}_1); 4.33 (dd, J = 12.1, 4.5 Hz, 1H, H^{II}_{6b}); 4.12 – 4.03 (m, 1H, H^{II}_5); 4.01 (ddd, J = 9.9, 6.7, 2.8 Hz, 1H, H^{III}_5); 3.92 (td, J = 9.3, 6.5 Hz, 2H, H^{I}_4, H^{II}_4); 3.72 (ddd, J = 9.7, 7.9, 2.5 Hz, 1H, H^{I}_5); 3.49 (s, 3H, -OC$\underline{H}_3$); 3.44 – 3.27 (m, 5H, -C$\underline{H}_2$S- Propargyl II, III, H^{III}_{6a}); 2.96 – 2.82 (m, 2H, H^{III}_{6b}, H^{I}_{6a}); 2.75 (dd, J = 14.4, 6.8 Hz, 1H, H^{I}_{6b}); 2.56 (t, J = 2.6 Hz, 1H, -C$\underline{H}$ Propargyl III); 2.24 (t, J = 2.6 Hz, 1H, -C$\underline{H}$ Propargyl II); 2.17 – 1.90 (m, 24H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 – 169.7 (8 x -$\underline{C}$OC$\underline{H}_3$); 101.1 (C^{I}_1); 95.5 (C^{II}_1); 95.2 (C^{III}_1); 80.0 (Cq I); 79.8 (Cq III); 75.6 (C^{I}_3); 75.4 (C^{I}_4); 74.0 (C^{I}_5); 72.7 (C^{II}_4, -$\underline{C}$H Propargyl III); 72.5 (C^{III}_2); 71.8 (C^{II}_3); 71.5 (-C$\underline{H}$ Propargyl I); 70.9 (C^{III}_5); 70.9 (C^{III}_4); 70.5 (C^{I}_2); 70.4 (C^{II}_2); 69.2 (C^{II}_5); 69.2 (C^{III}_3); 63.3 (C^{II}_6); 57.0 (-O$\underline{C}$H$_3$); 33.0 (C^{I}_6); 32.6 (C^{III}_6), 20.9 (-CH_2- Propargyl I); 20.3 (-CH_2- Propargyl III); 21.2 – 20.6 (8 x $CH_3\underline{C}$O-).

Synthesis of compound 41

To a solution of compound **37** (1.322 g; 1.499 mmol) in anhydrous DMF (53 mL) were added triethylamine (0.83 mL; 5.99 mmol) and dithiothreitol (0.46 g; 2.99 mmol) under an argon atmosphere. The mixture was stirred for a few minutes at room temperature and propargyl bromide was added dropwise (80 % in toluene; 0.814 mL; 7.497 mmol). After 6 h, reactants (Et3N, DTT and Propargyl bromide) were added in the same proportions. After 3 h of stirring, the reaction mixture was evaporated and diluted in toluene (30 mL). Then it was washed several times with a saturated solution of NaCl (30 mL) and finally with water. The organic phases were combined and dried over sodium sulfate, filtered and concentrated. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired product **41** as white crystals (1.12 g; 78 %). Rf: 0.39 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 75 °C; $[\alpha]_D^{20}$: +103.6 (c = 0.5 $CHCl_3$); IR (ATR): 1747.51; 1369.46; 1226.73; 1037.70 cm^{-1}; HRMS: Calcd. for $[C_{35}H_{54}NO_{22}S_2]$: m/z 980.2892 $[M+NH_4]^+$; Found 980.2909 $[M+NH_4]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 5.42 – 5.28 (m, 3H, H^{II}_3, H^{III}_1, H^{III}_3); 5.28 – 5.19 (m, 2H, H^{I}_1, H^{I}_3); 4.99 (t, *J* = 9.7 Hz, 1H, H^{III}_4); 4.86 – 4.76 (m, 2H, H^{III}_2, H^{I}_2); 4.70 (dd, *J* = 10.4, 4.0 Hz, 1H, H^{II}_2); 4.52 (dd, *J* = 12.1, 3.5 Hz, 1H, H^{I}_{6a}); 4.47 – 4.39 (m, 2H, H^{I}_1, H^{I}_{6b}); 4.14 – 4.03 (m, 2H, H^{III}_5, H^{II}_5); 3.95 (t, *J* = 9.2 Hz, 1H, H^{I}_4); 3.89 (t, *J* = 9.3 Hz, 1H, H^{II}_4); 3.70 (dt, *J* = 9.6, 4.1 Hz, 1H, H^{I}_5); 3.47 (s, 3H, -OC$\underline{H}_3$); 3.40 – 3.35 (m, 2H, -C$\underline{H}_2$S- Propargyl III); 3.32 (dd, *J* = 3.5, 2.6 Hz, 2H, -C$\underline{H}_2$S- Propargyl II); 3.21 (dd, *J* = 14.1, 2.7 Hz, 1H, H^{III}_{6a}); 3.00 (dd, *J* = 14.0, 7.4 Hz, 1H, H^{III}_{6b}); 2.94 (dd, *J* = 14.5, 3.0 Hz, 1H, H^{II}_{6a}); 2.76 (dd, *J* = 14.4, 6.8 Hz, 1H, H^{II}_{6b}); 2.38 (t, *J* = 2.5 Hz, 1H, -C$\underline{H}$ Propargyl III); 2.26 (t, *J* = 2.6 Hz, 1H; -C$\underline{H}$ Propargyl II); 2.15– 1.93 (m, 24H, C$\underline{H}_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 – 169.6 (8 x -$\underline{C}$OC$\underline{H}_3$); 101.2 (C^{I}_1); 95.4 (C^{II}_1); 95.4 (C^{III}_1); 80.0 – 79.9 (Cq II, III); 75.2 (C^{I}_3); 74.7 (C^{II}_4); 74.1 (C^{I}_4); 72.3 (C^{I}_5); 72.2 (C^{I}_2); 72.2 (CH Propargyl); 71.7 (C^{II}_3); 71.6 (CH Propargyl); 71.4

(C^{III}_5); 71.1 (C^{III}_4); 70.9 (C^{II}_5); 70.9 (C^{II}_2); 70.2 (C^{III}_2); 69.3 (C^{III}_3); 63.4 (C^{I}_6); 57.1 (-O<u>C</u>H$_3$);33.5 (C^{III}_6); 32.6;(C^{II}_6); 21.0 (-CH$_2$- Propargyl III); 20.9 (-CH$_2$- Propargyl II); 21.1 – 20.7 (8 x CH$_3$<u>C</u>O-).

Synthesis of compound 42

To a solution of compound **38** (0.499 g; 0.547 mmol) in anhydrous DMF (20 mL) were added triethylamine (0.3 mL; 2.188 mmol) and dithiothreitol (0.168 g; 1.09 mmol) under an argon atmosphere. The mixture was stirred for a few minutes at room temperature and propargyl bromide was added dropwise (80 % in toluene; 0.237 mL; 2.188 mmol). After 6 h, reactants (Et3N, DTT and Propargyl bromide) were added in the same proportions. After 3 h of stirring, the reaction mixture was evaporated and diluted in toluene (30 mL). Then it was washed several times with a saturated solution of NaCl (30 mL) and finally with water. The organic phases were combined and dried over sodium sulfate, filtered and concentrated. The residue was purified over silica gel chromatography (cyclohexane / ethyl acetate; 50 / 50; v / v) to lead to the desired product **42** as white crystals (0.492 g; 95 %). Rf: 0.25 (cyclohexane / ethyl acetate; 50 / 50; v / v); MP: 82 °C; $[\alpha]^{20}_D$: +93.2 (c = 0.5 $CHCl_3$); IR (ATR): 1745.58; 1699.29; 1226.73; 1037.70 cm^{-1}; HRMS: Calcd. for [$C_{40}H_{54}O_{24}NaS$]: m/z 973.2623 [M+Na]$^+$; Found 973.2623 [M+Na]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.43 – 5.29 (m, 3H, H^{II}_3, H^{III}_1, H^{III}_3); 5.29 – 5.20 (m, 2H, H^{II}_1, H^{I}_3); 5.02 (t, *J* = 9.7 Hz, 1H, H^{III}_4); 4.83 – 4.77 (m, 2H, H^{I}_2, H^{III}_2); 4.74 (dd, *J* = 10.4, 4.1 Hz, 1H, H^{II}_2); 4.52 – 4.46 (m, 1H, H^{I}_{6a}, H^{II}_{6a}); 4.45 – 4.42 (d, *J* = 8 Hz, 1H, H^{I}_1); 4.34 (dd, *J* = 12.1, 4.2 Hz, 1H, H^{I}_{6b}); 4.26 (dd, *J* = 12.2, 4.1 Hz, 1H, H^{II}_{6b}); 4.05 – 3.94 (m, 3H, H^{III}_5, H^{II}_5, H^{I}_4); 3.90 (dd, *J* = 8.0 Hz, 1H, H^{II}_4); 3.71 (ddd, *J* = 9.6, 4.2, 3.1 Hz, 1H, H^{I}_5); 3.48 (s, 3H, -OC<u>H</u>$_3$); 3.31 (t, *J* = 2.3 Hz, 2H, -C<u>H</u>$_2$S- Propargyl III); 2.87 (dd, *J* = 14.5, 3.0 Hz, 1H, H^{III}_{6a}); 2.74 (dd, *J* = 14.5, 6.7 Hz, 1H, H^{III}_{6b}); 2.24 (t, *J* = 2.6 Hz, 1H, -C<u>H</u> Propargyl III); 2.16 – 1.95 (m, 27H, C<u>H</u>$_3$CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 –169.7(9 x -<u>C</u>OCH$_3$); 101.2 (C^{I}_1); 95.8 (C^{I}_1); 95.4 (C^{III}_1); 80.0 (Cq III); 75.5(C^{I}_3); 74.0 (C^{I}_4); 73.0 (C^{II}_4); 72.3 (C^{I}_2); 72.2 (C^{I}_5); 71.7 (C^{I}_3); 71.5 (CH Propargyl); 71.0 (C^{III}_4); 70.8 (C^{III}_5); 70.6 (C^{II}_2); 70.5 (C^{III}_2); 69.3 (C^{III}_3); 69.2 (C^{II}_5); 63.1 (C^{II}_6); 63.0 (C^{I}_6); 57.1 (-O<u>C</u>H$_3$); 32.6 (C^{III}_6); 20.9 (-CH$_2$- Propargyl III); 21.2 – 20.7 (9 x CH$_3$<u>C</u>O-).

Synthesis of compound 43

To a solution of compounds **39** (150 mg; 0.160 mmol) and **21** (435 mg; 0.515 mmol) in a mixture of solvents dioxane/water (3.75 mL; 4/1), were added copper (II) sulfate pentahydrate (25.71 mg; 0.103 mmol) and sodium ascorbate (40.81 mg; 0.206 mmol). The mixture was stirred at 70 °C by microwaves. After 50 min. the reaction mixture was poured into a solution of H_2O/NH_4Cl (1/1; 30 mL), and then extracted using ethyl acetate (4 x 30 mL). The combined organic phases were dried over sodium sulfate, filtered and concentrated. The desired product **43** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 30 / 70; v / v) as white crystals (178 mg; 32 %). Rf: 0.55 (cyclohexane / ethyl acetate; 5 / 95; v / v); MP: 145 °C; $[\alpha]^{20}_D$: +27.4 (c = 0.5 $CHCl_3$); IR (ATR): 1741.72; 1369.46; 1240.23; 1224.80; 1039.63; 713.66 cm^{-1}; HRMS: Calcd. for [$C_{154}H_{182}N_9O_{70}S_6$]: m/z 3468.9283 [M+H]$^+$; Found 3468.9331 [M+H]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.81 (m, 12H, H_{aro}); 7.55 – 7.42 (m, 6H, H_{aro}); 7.41 – 7.34 (m, 12H, H_{aro}); 7.34 (s, 1H, -CH-triazole); 7.31 (s, 1H, -CH-triazole); 7.25 (s, 1H, -CH-triazole); 5.64 (dd, *J* = 11.3, 9.4 Hz, 3H, H_3); 5.41 – 5.31 (m, 4H, H_2, H^{III}_1); 5.31 – 5.23 (m, 5H, H^{II}_3, $H_{3'}$, H^{III}_3); 5.23 – 5.12 (m, 5H, H^{I}_3, H^{II}_1, $H_{4'}$); 4.99 (dd, *J* = 10.1, 2.0 Hz, 3H, $H_{1'}$); 4.93 – 4.80 (m, 5H, $H_{2'}$, H^{III}_2, H^{I}_2); 4.76 – 4.60 (m, 8H, H^{II}_2, H_{6a}, H_1); 4.56 (dd, *J* = 12.1, 4.1 Hz, 3H, H_{6b}); 4.44 (d, *J* = 7.9 Hz, 1H, H^{I}_1); 4.27 (ddt, *J* = 18.3, 13.5, 6.8 Hz, 6H, $H_{3''a,b}$); 4.19 – 4.07 (m, 4H, $H_{5'}$, H^{III}_5); 4.03 – 3.95 (m, 3H, H_5); 3.94 – 3.85 (m,7H, -SC<u>H</u>$_2$- triazole, $H_{1''a}$, H^{II}_5, H^{I}_4); 3.83 – 3.75 (m, 2H, H^{II}_4, -SC<u>H</u>$_2$- triazole); 3.75 – 3.56 (m, 12H, H^{I}_5, -COOC<u>H</u>$_3$, -SC<u>H</u>$_2$- triazole); 3.54 – 3.42 (m, 6H, -OC<u>H</u>$_3$, $H_{1''b}$, H^{III}_4); 3.26 (td, *J* = 10.9, 2.2 Hz, 3H, H_4); 3.21 – 3.01 (m, 2H, H^{II}_{6a}, H^{I}_{6a}); 2.95 (dd, *J* = 14.3, 7.6 Hz, 1H, H^{II}_{6b}); 2.76 (tdd, *J* = 15.3, 10.5, 5.7 Hz, 2H, $H^{III}_{6a,b}$); 2.15 – 1.5 (m, 56H, $H_{2''a,b}$, CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0 – 169.3 (18 x CH$_3$<u>C</u>O-); 166.6 (3 x -<u>C</u>OOCH$_3$); 165.8 – 165.3 (6 x -O<u>C</u>OBz); 145.5 –145.1 (3 x Cq); 133.6 – 128.6 (24 x C_{aro}); 122.9 –122.5 (3 x -<u>C</u>H-triazole); 101.4 (C^{I}_1); 101.1 – 100.1 (C_1); 95.7 (C^{II}_1); 95.5 (C^{III}_1); 81.4 – 81.4 (3 x $C_{1'}$); 76.6 (C^{I}_4); 75.7 (C^{I}_5); 75.5 ($C_{5'}$); 75.0 (C^{I}_3); 74.4 (C^{II}_4); 74.3, 74.2 (C_5) ; 73.5 – 73.4 (C_2); 73.2 (C^{II}_3) ; 73.1 ($C_{3'}$) ; 72.4 (C^{I}_2); 72.3 (C^{III}_4) 71.8 (C^{III}_3); 71.7 (C^{III}_5); 71.1 (C^{II}_5, C^{III}_2); 70.7 (C^{II}_2); 70.3 – 70.1 (C_3); 69.8 ($C_{2'}$); 69.1 ($C_{4'}$); 66.1 – 66.0 ($C_{1''}$); 63.5 (3 x C_6); 57.2 (-OCH$_3$); 53.1 (-<u>C</u>OOCH$_3$); 47.0 – 46.9 ($C_{3''}$); 46.3 – 46.3 (C_4); 34.2 (C^{I}_6); 33.8 (C^{II}_6); 33.7 (C^{III}_6); 30.3 – 30.0 ($C_{2''}$); 27.8 – 27.5 (-SC<u>H</u>$_2$- triazole); 21.2 – 20.03 (18 x CH$_3$<u>C</u>O-).

Synthesis of compound 44

To a solution of compounds **40** (100 mg; 0.103 mmol) and **21** (193 mg; 0.228 mmol) in a mixture of solvents dioxane/water (3.5 mL; 4/1), were added copper (II) sulfate pentahydrate (11.39 mg; 0.045 mmol) and sodium ascorbate (18.08 mg; 0.0912 mmol). The mixture was stirred at 70 °C by microwaves. After 50 min. the reaction mixture was poured into a solution of H_2O/NH_4Cl (1/1; 30 mL), and then extracted using ethyl acetate (4 x 30 mL). The combined organic phases were dried over sodium sulfate, filtered and concentrated. The desired product **44** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 30 / 70; v / v) as white crystals (135 mg; 50 %). Rf: 0.13 (cyclohexane / ethyl acetate; 20 / 80; v / v); MP: 128 °C; $[\alpha]^{20}_D$: +47.6 (c = 0.5 $CHCl_3$);

IR (ATR): 1743.65; 1369.47; 1222.87; 1224.80; 1037.70; 713.66 cm^{-1}; HRMS: Calcd. for $[C_{117}H_{140}N_6O_{56}S_4Na]$: m/z 2676.7104 $[M+Na]^+$; Found 2676.6296 $[M+Na]^+$; ^1H NMR (400 MHz, CDCl3): δ 7.94 (dq, *J* = 8.4, 1.3 Hz, 8H, H_{aro}); 7.58 – 7.44 (m, 4H, H_{aro}); 7.37 (dt, *J* = 9.5, 7.8 Hz, 8H, H_{aro}); 7.28 (s, 1H, -CH-triazole); 7.24 (s, 1H, -CH-triazole); 5.63 (dd, *J* = 11.2, 9.3 Hz, 2H, H_3); 5.41 – 5.32 (m, 4H, H_2, H^{II}_3, H^{III}_1); 5.32 – 5.28 (m, 1H, H^{III}_3); 5.28 – 5.21 (m, 4H, H^{III}_1, $H_{3'}$, H^{II}_1, H^{I}_3); 5.16 (t, *J* = 9.7 Hz, 2H, $H_{3'}$); 5.03 – 4.95 (m, 3H, H^{III}_4, $H_{1'}$); 4.89 (dd, *J* = 10.0, 9.0 Hz, 2H, $H_{2'}$); 4.85 – 4.71 (m, 3H, H^{I}_2, H^{II}_2, H^{III}_2); 4.70 – 4.61 (m, 4H, H_1, H_{6a}); 4.55 (dd, *J* = 12.1, 4.1 Hz, 2H, H_{6b}); 4.49 – 4.39 (m, 2H, H^{II}_{6a}, H^{I}_1); 4.27 (m, 5H, $H_{3''a,b}$, H^{II}_{6b}); 4.18 – 4.09 (m, 2H, $H_{5'}$); 4.08 – 4.01 (m, 2H, H^{I}_4); 4.01 – 3.83 (m, 7H, H^{III}_5, H_5, H^{II}_5, H^{II}_4, $H_{1'a}$); 3.83 – 3.67 (m, 11H, H^{I}_5, -COOC<u>H</u>$_3$, -SC<u>H</u>$_2$- triazole); 3.48 (s, 5H, $H_{1'b}$, -OC<u>H</u>$_3$); 3.25 (t, *J* = 10.9 Hz, 2H, H_4); 3.12 (dd, *J* = 14.6, 2.9 Hz, 1H, H^{I}_{6a}); 2.87 (dd, *J* = 14.6, 5.9 Hz, 1H, H^{I}_{6b}); 2.76 (dd, *J* = 14.3, 3.0 Hz, 1H, H^{III}_{6a}); 2.59 (dd, *J* = 14.2, 6.1 Hz, 1H, H^{III}_{6b}); 2.25 – 1.53 (m, 52H, $H_{2''a,b}$, CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 – 169.3 (16 x CH_3<u>C</u>O-); 166.6 (2 x -<u>C</u>OOCH$_3$); 165.8 – 165.3 (4 x -O<u>C</u>OBz); 145.5 – 145.3 (2 x Cq) 133.6 – 128.5 (24 x C_{aro}); 122.5 (2 x -<u>C</u>H-triazole); 101.2 (C^{I}_1); 101.0 (C_1); 95.7 (C^{II}_1); 95.5 (C^{III}_1); 81.3 ($C_{1'}$); 75.5 ($C_{5'}$, C^{I}_3); 75.4 (C^{I}_4); 75.1 (C^{I}_3); 74.3 (C^{I}_5); 74.2 (C_5); 73.4 (C_2); 73.1 ($C_{3'}$); 72.9 (C^{II}_5); 72.4 (C^{I}_2); 71.9 (C^{II}_3); 70.7 (C^{III}_4); 70.6 (C^{III}_5); 70.5 (C^{II}_2); 70.3 (C^{III}_2); 70.1 (C_3); 69.8 ($C_{2'}$); 69.5 (C^{III}_3); 69.2 (C^{II}_4); 69.0 ($C_{4'}$); 66.1 – 66.0 (2 x $C_{1''}$); 63.4 (C_6); 63.2 (C^{II}_6); 57.1 (-O<u>C</u>H$_3$); 53.1 (-<u>C</u>OOCH$_3$); 46.8 ($C_{3''}$); 46.3 (C_4); 33.5 (C^{I}_6); 32.8 (C^{III}_6); 30.3 – 30.2(2 x $C_{2''}$); 27.8 – 27.2 (2 x -S<u>C</u>H$_2$- triazole); 21.1 – 20.6 (16 x <u>C</u>H$_3$CO-).

Synthesis of compound 45

To a solution of compounds **41** (150 mg; 0.155 mmol) and **21** (276 mg; 0.327 mmol) in a mixture of solvents dioxane/water (3.5 mL; 4/1), were added copper (II) sulfate pentahydrate (16.35 mg; 0.0654 mmol) and sodium ascorbate (26 mg; 0.130 mmol). The mixture was stirred at 70 °C by microwaves. After 50 min. the reaction mixture was poured into a solution of H_2O/NH_4Cl (1/1; 30 mL), and then extracted using ethyl acetate (4 x 30 mL). The combined organic phases were dried over sodium sulfate, filtered and concentrated. The desired product **45** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 30 / 70; v / v) as white crystals (150 mg; 36 %). Rf: 0.32 (cyclohexane / ethyl acetate; 10 / 90; v / v); MP: 132 °C; $[\alpha]_D^{20}$: +27.8 (c = 0.5 $CHCl_3$); IR (ATR): 1743.65; 1369.46; 1240.23; 1224.80; 1037.70; 713.66 cm^{-1}; HRMS: Calcd. for $[C_{117}H_{140}N_6O_{56}S_4]$: m/z 1327.8656 $[M+2H]^{2+}$; Found 1327.8682 $[M+2H]^{2+}$; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (ddd, *J* = 8.2, 2.8, 1.3 Hz, 8H, H_{aro}); 7.51 (qt, *J* = 8.5, 1.3 Hz, 4H, H_{aro}); 7.39 (dd, *J* = 9.6, 6.6 Hz, 8H, H_{aro}); 7.34 (s, 1H, -CH-triazole); 7.30 (s, 1H, -CH-triazole); 5.64 (dd, *J* = 11.2, 9.4 Hz, 2H, H_3); 5.41 – 5.31 (m, 5H, H^{II}_3, H_2, H^{III}_1); 5.31 – 5.21 (m, 5H, H^{III}_3, H^{I}_3, H^{II}_1, $H_{3'}$); 5.17 (td, *J* = 9.7, 1.1 Hz, 2H, $H_{4'}$); 4.99 (m, H^{III}_4, $H_{1'}$); 4.96 – 4.87 (m, 2H, $H_{2'}$); 4.85 – 4.75 (m, 2H, H^{II}_2, H^{III}_2); 4.73 – 4.61 (m, 5H, H^{II}_2, H_{6a}, H_1); 4.60 – 4.39 (m, 4H, H_{6b}, H^{I}_1, $H^{I}_{6a,b}$); 4.28 (q, *J* = 7.2 Hz, 4H, $H_{3''a,b}$); 4.15 (dd, *J* = 10.0, 5.0 Hz, 2H, $H_{5'}$); 4.09 – 3.80 (m, 10H, H^{II}_5, H_5, H^{III}_5, H^{I}_4, H^{II}_4, $H_{1'a}$, -SC<u>H</u>$_2$- triazole); 3.73 (s, 9H, -COOC<u>H</u>$_3$, H^{I}_5, -SC<u>H</u>$_2$- triazole); 3.55 – 3.44 (m, 5H, -OC<u>H</u>$_3$, $H_{1''b}$); 3.26 (t, *J* = 10.9 Hz, 2H, H_4); 3.05 – 2.98 (m, 1H, H^{II}_{6a}); 2.94 (dd, *J* = 14.1, 6.9 Hz, 1H, H^{II}_{6b}); 2.84 (dd, *J* = 14.2, 3.0 Hz, 1H, H^{III}_{6a}); 2.61 (dd, *J* = 14.3, 6.2 Hz, 1H, H^{III}_{6b}); 2.24 – 1.54 (m, 52H, $H_{2''a,b}$, CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 – 169.4 (16 x CH_3<u>C</u>O-); 166.6 (2 x -<u>C</u>OOCH$_3$); 165.7 –165.3 (4 x -O<u>C</u>OBz); 145.4 – 145.1 (2 x Cq); 133.6 – 128.6 (24 x C_{aro}); 122.8 (2 x -<u>C</u>H-triazole); 101.3 (C^{I}_1); 101.1 – 101.0 (C_1); 95.6 (C^{II}_1); 95.5 (C^{III}_1); 81.4 – 81.3 ($C_{1'}$); 75.5 ($C_{5'}$); 75.2 (C^{I}_3); 75.0 (C^{I}_4); 74.4 (C^{III}_5); 74.3 (C_5); 73.4 (C_2); 73.1 ($C_{3'}$); 72.3 (C^{I}_5); 72.3 (C^{I}_2); 71.8 (C^{II}_3); 71.4 (C^{II}_5); 71.1 (C^{III}_2); 70.8 (C^{II}_4); 70.7 (C^{III}_4); 70.3 (C^{II}_2); 70.2 (C_3); 69.8 ($C_{2'}$); 69.5 (C^{III}_3); 69.1 ($C_{4'}$); 66.2 – 66.0 ($C_{1''}$); 63.7 (C^{I}_6); 63.5 (C_6); 57.1 (-O<u>C</u>H$_3$); 53.1 (-<u>C</u>OOCH$_3$); 47.0 – 46.9 ($C_{3''}$); 46.3 (C_4); 34.2 (C^{II}_6); 32.8 (C^{III}_6); 30.2 ($C_{2''}$); 27.8 – 27.2 (-S<u>C</u>H$_2$- triazole); 21.2 – 20.0 (16 x <u>C</u>H$_3$CO-).

Synthesis of compound 46

To a solution of compounds **42** (150 mg; 0.157 mmol) and **21** (146 mg; 0.173 mmol) in a mixture of solvents dioxane/water (3.5 mL; 4/1), were added copper (II) sulfate pentahydrate (8.619 mg; 0.0345 mmol) and sodium ascorbate (13.67 mg; 0.069 mmol). The mixture was stirred at 70 °C by microwaves. After 50 min. the reaction mixture was poured into a solution of H_2O/NH_4Cl (1/1; 60 mL), and then extracted using ethyl acetate (4 x 30 mL). The combined organic phases were dried over sodium sulfate, filtered and concentrated. The desired product **46** was obtained after purification over silica gel chromatography (cyclohexane / ethyl acetate; 20 / 80; v / v) as white crystals (204 mg; 72 %). Rf: 0.29 (cyclohexane / ethyl acetate; 20 / 80; v / v); MP: 126 °C; $[\alpha]_D^{20}$: +50.2 (c = 0.5 $CHCl_3$); IR (ATR): 1743.65; 1369.46; 1224.80; 1037.70; 713.66 cm^{-1}; HRMS: Calcd. for $[C_{78}H_{97}N_3O_{41}NaS_2]$: m/z 1818.4937 $[M+Na]^+$; Found 1818.4941 $[M+Na]^+$; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (ddd, *J* = 8.5, 2.7, 1.3 Hz, 4H, H_{aro}); 7.62 – 7.44 (m, 2H, H_{aro}); 7.38 (dt, *J* = 10.7, 7.8 Hz, 4H, H_{aro}); 7.26 (S, 1H, -CH-triazole); 5.63 (dd, *J* = 11.3, 9.4 Hz, 1H, H_3); 5.44 – 5.32 (m, 3H, H_2, H^{II}_3, H^{III}_1); 5.32 – 5.20 (m, 4H, $H_{3'}$, H^{II}_1, H^{III}_3, H^{I}_3); 5.17 (t, *J* = 9.7 Hz, 1H, $H_{3'}$); 5.05 – 4.95 (m, 2H, $H_{1'}$, H^{III}_4); 4.89 (dd, *J* = 10.0, 8.9 Hz, 1H, $H_{2'}$); 4.83 – 4.77 (m, 2H, H^{II}_2, H^{I}_2); 4.74 (dd, *J* = 10.3, 4.1 Hz, 1H, H^{III}_2); 4.70 – 4.61 (m, 2H, H_1, H_{6a}); 4.55 (dd, *J* = 12.1, 4.1 Hz, 1H, H_{6b}); 4.45 (m, 3H, H^{I}_{6a}, H^{I}_1, H^{II}_{6a}); 4.35 (dd, *J* = 12.1, 4.1 Hz, 1H, H^{I}_{6b}); 4.27 (dd, *J* = 7.6, 5.4 Hz, 3H, $H_{3''a,b}$, H^{II}_{6b}); 4.18 – 4.06 (m, 1H, $H_{5'}$); 4.04 – 3.80 (m, 6H, H^{I}_5, H_5, H^{I}_4, H^{III}_5, H^{II}_4, $H_{1''a}$); 3.73 (m, 6H, -COOC<u>H</u>$_3$, -SC<u>H</u>$_2$- triazole, H^{II}_5); 3.48 (m, 4H, -OC<u>H</u>$_3$, $H_{1''b}$); 3.26 (t, *J* = 10.9 Hz, 1H, H_4); 2.77 (dd, *J* = 14.2, 3.0 Hz, 1H, H^{III}_{6a}); 2.61 (dd, *J* = 14.2, 6.4 Hz, 1H, H^{III}_{6b}); 2.22 – 1.53 (m, 41H, $H_{2''a,b}$, CH_3CO-). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7 –

169.3 (13 x $CH_3\underline{C}O$-);166.6 (-$\underline{C}OOCH_3$); 165.8 – 165.3 (2 x -O$\underline{C}$OBz); 145.5 (Cq triazole); 133.6 – 128.6 (12 C_{aro}); 122.6 (-CH-triazole); 101.2 (C^{I}_1); 101.1 (C_1); 95.8 (C^{II}_1); 95.5 (C^{III}_1); 81.4 ($C_{1'}$); 75.5 ($C_{5'}$); 75.4 (C^{I}_3); 74.3 (C_5); 74.1 (C^{I}_4); 73.4 (C_2); 73.1 ($C_{3'}$); 73.0 (C^{II}_4); 72.3 (C^{I}_2); 72.2 (C^{I}_5); 71.8 (C^{II}_3); 70.7 (C^{III}_4, C^{III}_5); 70.6 (C^{II}_2); 70.4 (C^{III}_2); 70.1 (C_3); 69.8 ($C_{2'}$); 69.4 (C^{III}_3); 69.1 (C^{II}_5); 69.1 ($C_{4'}$); 65.9 ($C_{1''}$); 63.4 (C_6); 63.2 (C^{I}_6); 63.1(C^{II}_6); 57.1 (-O$\underline{C}H_3$) ; 53.1 (-$\underline{C}OOCH_3$); 46.8 ($C_{3''}$); 46.3 (C_4); 32.7 (C^{III}_6); 30.2 ($C_{2''}$); 27.1 (-S$\underline{C}H_2$- triazole); 21.1 – 20.0 (13 x $\underline{C}H_3CO$-).

Synthesis of compound 47

To a solution of compound **43** (70 mg; 0.0201 mmol) in methanol/water (6 mL; 5/1) at 0 °C, was added dropwise a solution of NaOH (3 M; 2 mL; 6 mmol). The reaction mixture was then stirred 10 min. at 0 °C and 6 h at room temperature. Then a diluted solution of HCl (1 M) was added in order to obtain a pH = 8 (using a pH-meter). The mixture was concentrated and the residue purified over sephadex™ LH-20. The desired product **47** was obtained after freeze-drying as a cottony white solid (41 mg; 95 %). MP: 225 °C; $[\alpha]^{20}_D$: -12.0 (c = 0.5 H_2O); IR (ATR): 3336.9; 2887.4;1608.6; 1413.8; 1056.9 cm^{-1}; HRMS: Calcd. for $[C_{73}H_{115}N_9O_{46}S_6]$: m/z 1021.7552 $[M\text{-}3Na+H]^{2-}$; Found 1021.7511 $[M\text{-}3Na+H]^{2-}$; ^{1}H NMR (400 MHz, D_2O) δ 7.96 – 7.93 (s, 3H, 3 x -CH-triazole); 5.35 (d, *J* = 4.0 Hz, 1H, H^{III}_1); 5.31 (d, *J* = 3.8 Hz, 1H, H^{II}_1); 4.64 (d, *J* = 9.8 Hz, 3H, $H_{1'}$); 4.59 – 4.45 (m, 6H, $H_{3''a,b}$); 4.40 (m, 4H, H_1, H^{I}_1); 4.08 (dd, *J* = 12.5, 2.1 Hz, 3H, H_{6a}); 4.00 – 3.80 (m, 15H, H_{6b}, H^{II}_3, H^{III}_3, H^{I}_5, $H_{1''a}$, -S$\underline{C}H_2$- triazole); 3.75 (m, 5H, H^{III}_5, H^{I}_3, $H_{4'}$); 3.71 – 3.46 (m, 24H, H^{II}_5, H^{III}_2, H^{II}_2, H_5, $H_{1''b}$, -OC$\underline{H}_3$, H_3, $H_{3'}$, H^{I}_4, $H_{5'}$, H^{III}_4, H^{II}_4); 3.46 – 3.37 (m, 3H, $H_{2'}$); 3.37 – 3.27 (m, 4H, H_2, H^{I}_2); 3.19 (dd, *J* = 14.3, 2.5 Hz, 1H, H^{II}_{6a}); 3.05 (dd, *J* = 14.0, 2.4 Hz, 1H, H^{I}_{6a}); 2.96 – 2.85 (m, 4H, H_4, H^{III}_{6a}); 2.85 – 2.72 (m, 1H, H^{I}_{6b}); 2.67 (dd, *J* = 14.0, 8.6 Hz, 1H, H^{III}_{6b}); 2.19 (h, *J* = 5.4, 4.2 Hz, 6H, $H_{2''a,b}$).^{13}C NMR (101 MHz, D_2O) δ 175.6 (3 x -$\underline{C}$OONa); 145.2 – 144.9 (3 x Cq triazole); 124.3 (-CH-triazole); 103.2 (C^{I}_1); 102.0 (C_1); 100.4 (C^{II}_1); 99.9 (C^{III}_1); 83.9 ($C_{1'}$); 81.5 (C^{I}_4); 81.2 (C^{II}_4); 79.5 ($C_{4'}$); 76.7 ($C_{3'}$); 76.5 (C_5); 76.0 (C^{I}_3); 74.2 (C_2); 74.1 –71.4 (9 x –CH- maltotriose (C^{I}_2, C^{I}_5, C^{II}_2, C^{II}_3,C^{II}_5, C^{III}_2, C^{III}_3 C^{III}_4 C^{III}_5)); 71.23 (C_3); 72.2 ($C_{2'}$); 71.6 ($C_{5'}$); 66.3 ($C_{1''}$); 61.2 (C_6); 57.2 (-O$\underline{C}H_3$); 47.1 ($C_{3''}$); 46.9 (C_4); 33.1 (C^{II}_6, C^{I}_6); 32.7 (C^{III}_6); 29.6($C_{2''}$); 26.2 (-S$\underline{C}H_2$- triazole I); 26.0 (-S$\underline{C}H_2$- triazole III); 25.9 (-S$\underline{C}H_2$- triazole II).

Synthesis of compound 48

To a solution of compound **44** (53.1 mg; 0.020 mmol) in methanol/water (6 mL; 5/1) at 0 °C, was added dropwise a solution of NaOH (3 M; 2 mL; 6 mmol). The reaction mixture was then stirred 10 min. at 0 °C and 6 h at room temperature. Then a diluted solution of HCl (1 M) was added in order to obtain a pH = 8 (using a pH-meter). The mixture was concentrated and the residue purified over sephadex™ LH-20. The desired product **48** was obtained after freeze-drying as a cottony white solid (41.7 mg; 83 %). MP: 212 °C; $[\alpha]^{20}_D$: + 9,6 (c = 0.5 H_2O); IR (ATR): 3371.6; 2883.6; 1608.6; 1413.75; 1145.7; 1055.1 cm^{-1}; HRMS: Calcd. for $[C_{55}H_{88}N_6O_{36}S_2]$: m/z 767.6898 $[M\text{-}2Na]^{2-}$; Found 767.1966 $[M\text{-}2Na]^{2-}$; ^{1}H NMR (400 MHz, D_2O) δ 8.00 (s, 2H, 2 x -CH-triazole); 5.41 (d, *J* = 4.0 Hz, 1H, H^{III}_1); 5.27 (d, *J* = 3.7 Hz, 1H, H^{II}_1); 4.64 (d, *J* = 9.8 Hz, 2H, $H_{1'}$); 4.61 – 4.46 (m, 4H, $H_{3''}$ a,b); 4.44 – 4.40 (2d, 2H, H_1); 4.37 (d, *J* = 8.0 Hz, 1H, H^{I}_1); 4.17 – 3.23 (m, 41H, H_{6b}, -S$\underline{C}H_2$- triazole, $H_{1''a,b}$, $H^{I}_{6a,b,,}$ H^{I}_3, H^{I}_4, H^{I}_5, H^{II}_2, H^{II}_3, H^{II}_4, H^{II}_5, H^{III}_2, H^{III}_3, H^{III}_4, H^{III}_5, $H_{4'}$, H_5, -O$\underline{C}H_3$, H_3, $H_{5'}$, $H_{3'}$, $H_{2'}$, H^{I}_2, H_2); 3.13 – 2.57 (m, 4H, H^{I}_{6a}, H^{III}_{6a}, H^{I}_{6b}, H^{III}_{6b}); 2.89 (t, *J* = 10.8 Hz, 2H, H_4); 2.23 (d, *J* = 8.5 Hz, 4H, $H_{2''a,b}$). ^{13}C NMR (101 MHz, D_2O) δ 175.6 (2 x -$\underline{C}$OONa); 145.2 (2 x Cq triazole); 124.4 (2 x -CH-triazole); 103.1 (C^{I}_1); 101.9 (C_1); 100.3 (C^{II}_1); 99.4 (C^{III}_1); 83.8 ($C_{1'}$); 79.9 ($C_{4'}$),76.8 ($C_{3'}$); 76.5 (C_5); 74.23, 73.2 (C_2); 72.7 (C_3); 72.2 ($C_{2'}$); 71.6 ($C_{5'}$); 78.4 -71.3 (12 –CH- maltotriose (C^{I}_2 , C^{I}_3, C^{I}_4 ,C^{I}_5, C^{II}_2, C^{II}_3,C^{II}_4, C^{II}_5, C^{III}_2, C^{III}_3 C^{III}_4 C^{III}_5)); 66.3 ($C_{1''}$); 61.2 (C_6); 60.6 (C^{II}_6); 57.2 (-O$\underline{C}H_3$); 47.2 ($C_{3''}$); 46.9 (C_4); 32.7 (C^{I}_6, C^{III}_6); 29.6 ($C_{2''}$); 26.0 (2 x -S$\underline{C}H_2$- triazole).

Synthesis of compound 49

To a solution of compound **45** (800 mg; 0.031 mmol) in methanol/water (6 mL; 5/1) at 0 °C, was added dropwise a solution of NaOH (3 M; 2 mL; 6 mmol). The reaction mixture was then stirred 10 min. at 0 °C and 6 h at room temperature. Then a diluted solution of HCl (1 M) was added in order to obtain a pH = 8 (using a pH-meter). The mixture was concentrated and the residue purified over sephadex™ LH-20. The desired product **49** was obtained after freeze-drying as a cottony white solid (46 mg; 96 %). MP: 218 °C; $[\alpha]^{20}_D$: + 5,6 (c = 0.5 H_2O); IR (ATR): 3390.86; 1608.63; 1415.75; 1149.57; 1060.85; 1039.63 cm^{-1}; HRMS: Calcd. for $[C_{55}H_{88}N_6O_{36}S_2]$: m/z 767.1983 $[M\text{-}2Na]^{2-}$; Found 767.1966 $[M\text{-}2Na]^{2-}$; ^{1}H NMR (400 MHz, D_2O) δ 8.18 – 7.86 (s, 2H, 2 x -CH-triazole); 5.48 – 5.25 (m, 2H, H^{II}_1, H^{III}_1); 4.64 (d, *J* = 9.7 Hz, 2H, $H_{1'}$); 4.54 (qd, *J* = 13.2, 11.8, 6.3 Hz, 4H, $H_{3''a,b}$); 4.41 (2d, *J* = 8.2, 5.8 Hz, 2H, H_1, H^{I}_1); 4.13 – 4.02 (m, 2H, H_{6a}); 4.02 – 3.27 (m, 41H, H_{6b}, -S$\underline{C}H_2$- triazole, $H_{1''a,b}$, $H^{I}_{6a,b,,}$ H^{I}_3, H^{I}_4, H^{I}_5, H^{II}_2, H^{II}_3, H^{II}_4, H^{II}_5, H^{III}_2, H^{III}_3, H^{III}_4, H^{III}_5, $H_{4'}$, H_5, -O$\underline{C}H_3$, H_3, $H_{5'}$, $H_{3'}$, $H_{2'}$, H^{I}_2, H_2); 3.36 (m, 3H, H_2, H^{I}_2); 3.18 – 2.58 (m, 6H, H^{II}_{6a}, H^{III}_{6a}, H_4, H^{II}_{6b}, H^{III}_{6b}); 2.31 – 2.06 (m, 4H, $H_{1''a,b}$); ^{13}C NMR (101 MHz, D_2O) δ 175.7 (2 x -$\underline{C}$OONa); 145.2 (2 x Cq triazole); 124.5 (2 x -CH-triazole) 103.2 (C^{I}_1); 102.0 (C_1); 100.4 (C^{II}_1); 99.8 (C^{III}_1); 83.9 ($C_{1'}$); 81.1-70.7 (11 –CH- maltotriose (C^{I}_2 , C^{I}_4 ,C^{I}_5, C^{II}_2, C^{II}_3,C^{II}_4, C^{II}_5, C^{III}_2, C^{III}_3 C^{III}_4 C^{III}_5)); 79.7 ($C_{4'}$); 76.9 ($C_{3'}$); 76.6 (C_5); 76.2 (C^{I}_3); 74.3 (C_2); 73.3 (C_3); 72.3 ($C_{2'}$); 71.7 ($C_{5'}$); 66.4 ($C_{1''}$); 61.3 (C_6); 61.2 (C^{I}_6); 57.3 (-O$\underline{C}H_3$); 47.0 ($C_{3''}$); 47.0 (C_4) 33.6 (C^{II}_6); 33.1 (C^{III}_6); 29.7 ($C_{2''}$); 26.5 (2 x -S$\underline{C}H_2$- triazole).

Synthesis of compound 50

To a solution of compound **46** (70 mg; 0.039 mmol) in methanol/water (6 mL; 5/1) at 0 °C, was added dropwise a solution of NaOH (3 M; 2 mL; 6 mmol). The reaction mixture was then stirred 10 min. at 0 °C and 6 h at room temperature. Then a diluted solution of HCl (1 M) was added in order to obtain a pH = 8 (using a pH-meter). The mixture was concentrated and the residue purified over sephadex™LH-20. The desired product **50** was obtained after freeze-drying as a white solid (38.7 mg; 94 %). MP: 188 °C; $[\alpha]_D^{20}$: + 36 (c = 0.5 H_2O); IR (ATR): 3307.9; 1610.6; 1411.9; 1031.9 cm^{-1}; HRMS: Calcd. for [$C_{37}H_{60}N_3O_{26}S_2$]: m/z 1026.2906 [M-Na]-; Found 1026.2886 [M-Na]-; ^{1}H NMR (400 MHz, D_2O): δ 7.99 (s, 1H, -CH-triazole); 5.40 (d, *J* = 3.9 Hz, 1H, H^{III}_1); 5.33 (d, *J* = 3.7 Hz, 1H, H^{II}_1); 4.65 (d, *J* = 9.8 Hz, 1H, $H_{1'}$); 4.56 (t, *J* = 6.8 Hz, 2H, $H_{3'',a,b}$); 4.42 (2d, *J* = 8.0 Hz, 2H, H_1, H^{I}_1); 4.10 (dd, *J* = 12.4, 2.1 Hz, 1H, H_{6a}); 4.02 – 3.25 (m, 31H, H_{6b}, -SC<u>H</u>$_2$- triazole, $H_{1'',a,b}$, $H^{I}_{6a,b}$,, $H^{II}_{6a,b}$, H^{I}_3, H^{I}_4, H^{I}_5, H^{II}_2, H^{II}_3, H^{II}_4, H^{II}_5, H^{III}_2, H^{III}_3, H^{III}_4, H^{III}_5, $H_{4'}$, H_5, -OC<u>H</u>$_3$, H_3, $H_{5'}$,, $H_{3'}$, $H_{2'}$, H^{I}_2, H_2); 2.99 (dd, *J* = 14.3, 2.5 Hz, 1H, H^{III}_{6a}); 2.90 (t, *J* = 9.1 Hz, 1H, H_4); 2.72 (dd, *J* = 14.3, 8.0 Hz, 1H, H^{III}_{6b}); 2.24 (p, *J* = 6.7 Hz, 2H, $H_{2'',a,b}$). ^{13}C NMR (101 MHz, D_2O): δ 175.6 (-<u>C</u>OONa); 145.0 (Cq triazole); 124.4 (-CH-triazole); 103.1 (C^{I}_1); 101.9 (C_1); 100.0 (C^{II}_1); 99.5 (C^{III}_1); 83.7 ($C_{1'}$); 79.6 ($C_{4'}$); 77.7-71.3 (C_2, C_3, C_5, $C_{2'}$, $C_{3'}$, $C_{4'}$, $C_{5'}$, C^{I}_2, C^{I}_3 C^{I}_4 C^{I}_5, C^{II}_2, C^{II}_3 C^{II}_4 C^{II}_5, C^{III}_2, C^{III}_3 C^{III}_4 C^{III}_5); 66.3 ($C_{1''}$); 61.2 (C_6); 60.8 (C^{I}_6); 60.7 (C^{II}_6); 57.2 (-O<u>C</u>H$_3$); 47.2 ($C_{3''}$); 46.9 (C_4); 32.6 (C^{III}_6); 29.6 ($C_{2''}$); 26.0 (-S<u>C</u>H$_2$- triazole).

Synthesis of compound 51

To a solution of compound **17β** (100 mg; 0.128 mmol) in methanol/H_2O (6 mL; 5/1) was slowly added a solution of NaOH (3 M; 2 mL; 6 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min. and then 6 h at room temperature. A 1 M solution of HCl was added until a pH = 8 was reached (using a pH-meter). The reaction mixture was then concentrated under reduced pressure and the desired product purified over sephadex™ LH-20. Compound **51** was obtained as white crystals (32.2 mg; 61 %). MP: 216 °C; $[\alpha]_D^{20}$: +19.4 (c = 0.5 H_2O); IR (ATR): 3313.7; 1606.7; 1415.6; 1138; 1062.8; 1041.6 cm^{-1}; HRMS: Calcd. for [$C_{13}H_{21}O_{11}NaS$]: m/z 409.0781 [M+Na]$^+$; Found 409.0771 [M+Na]$^+$; ^{1}H NMR (400 MHz, D_2O) δ 4.86 (d, *J* = 3.7 Hz, 1H, H_1); 4.65 (d, *J* = 9.8 Hz, 1H, $H_{1'}$); 4.01 (m, 2H, $H_{6a,b}$); 3.89 (dt, *J* = 11.3, 3.2 Hz, 1H, H_5); 3.83 – 3.68 (m, 2H, H_3, $H_{4'}$); 3.62 (dd, *J* = 9.5, 3.7 Hz, 1H, H_2); 3.58 – 3.47 (m, 2H, $H_{5'}$, $H_{3'}$); 3.41 (s, 4H, $H_{2'}$, -OC<u>H</u>$_3$); 2.90 (t, *J* = 10.9 Hz, 1H, H_4). ^{13}C NMR (101 MHz, D_2O) δ 175.7 (-COONa); 99.4 (C_1); 83.7 ($C_{1'}$); 79.9 ($C_{4'}$); 77.0 ($C_{5'}$); 72.5 (C_2); 72.3 ($C_{2'}$); 72.1 (C_5); 71.8 ($C_{3'}$); 69.9 (C_3); 61.2 (C_6); 55.1 (-O<u>C</u>H$_3$) 46.8 (C_4).

Notes and references

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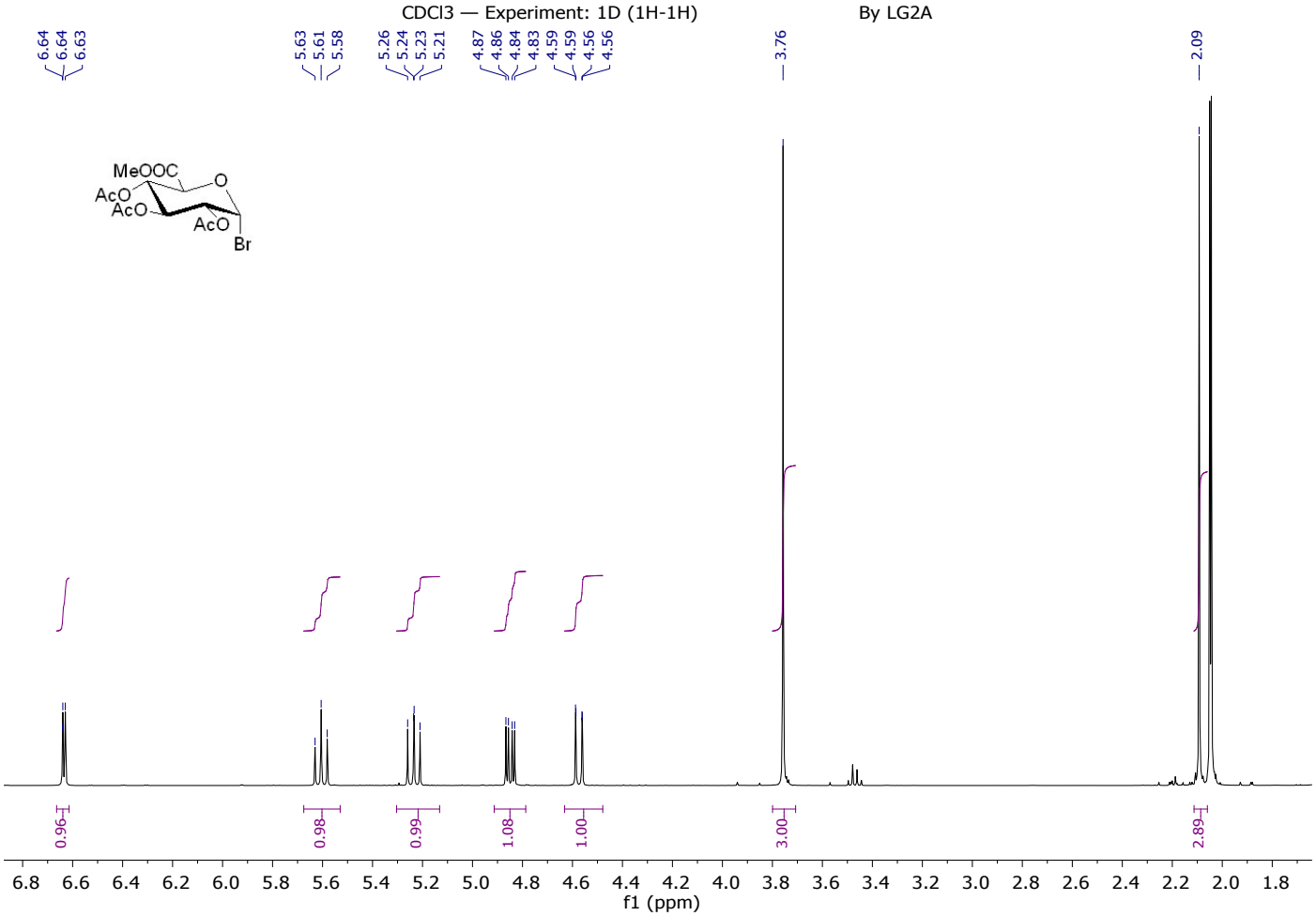
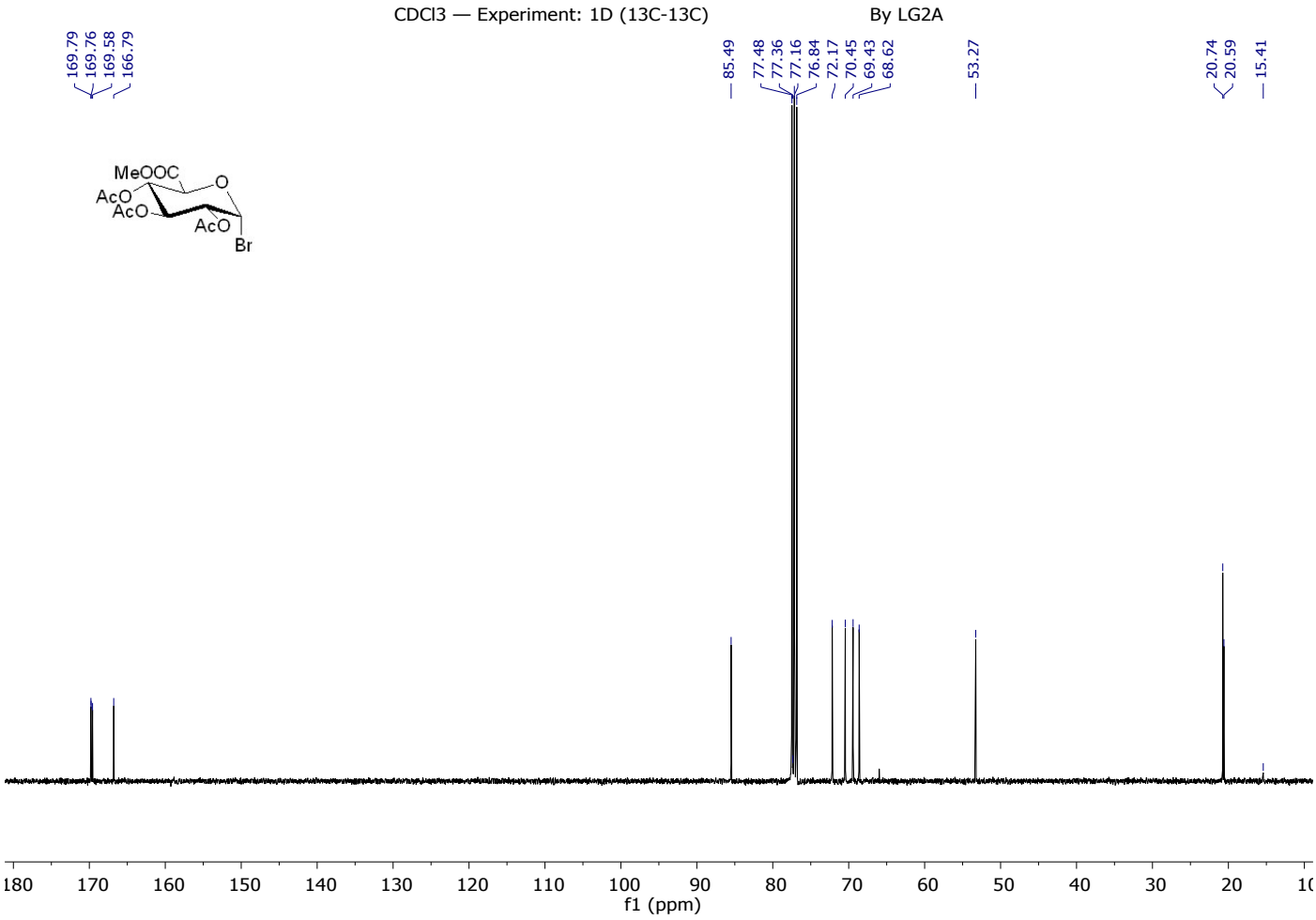
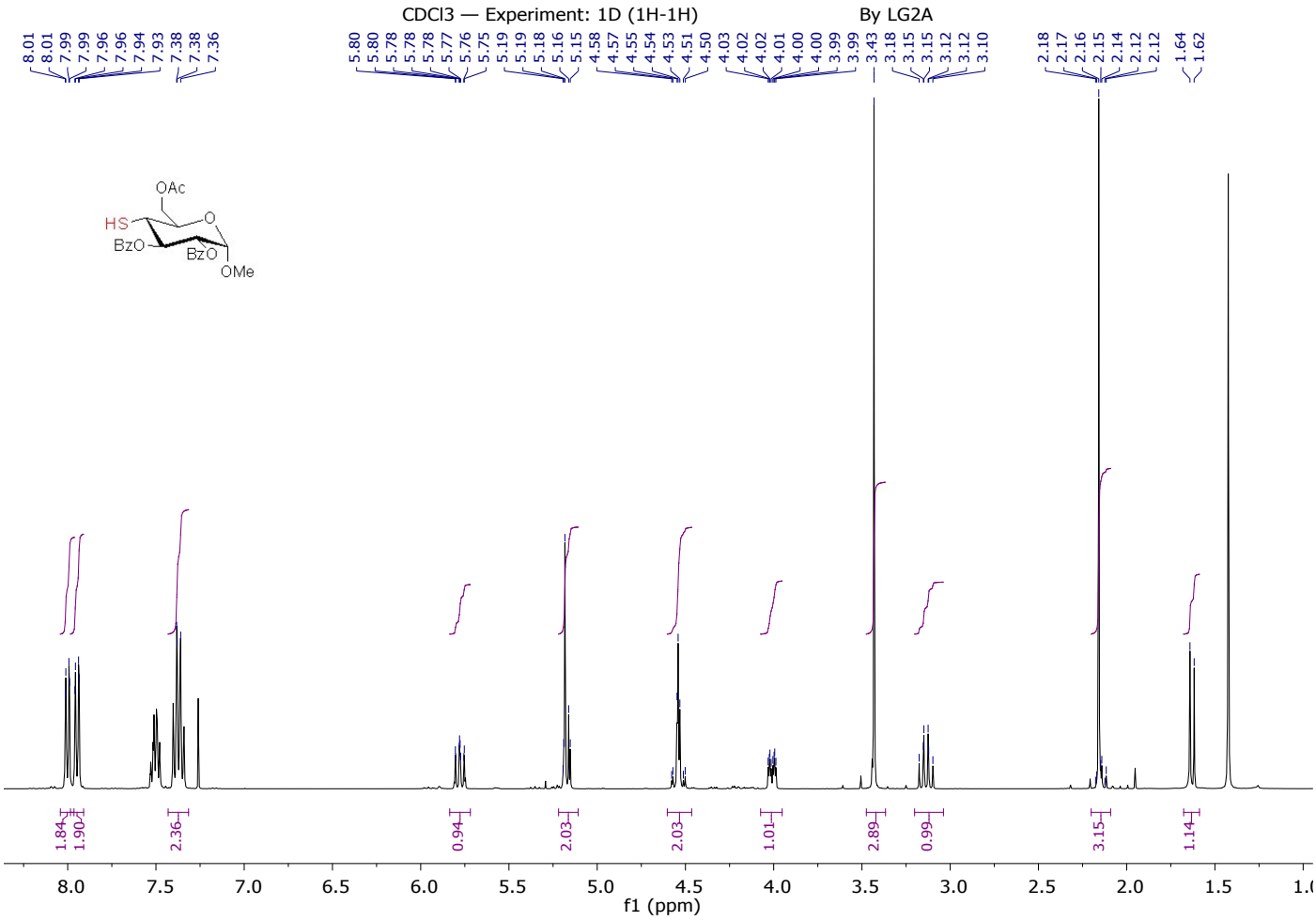
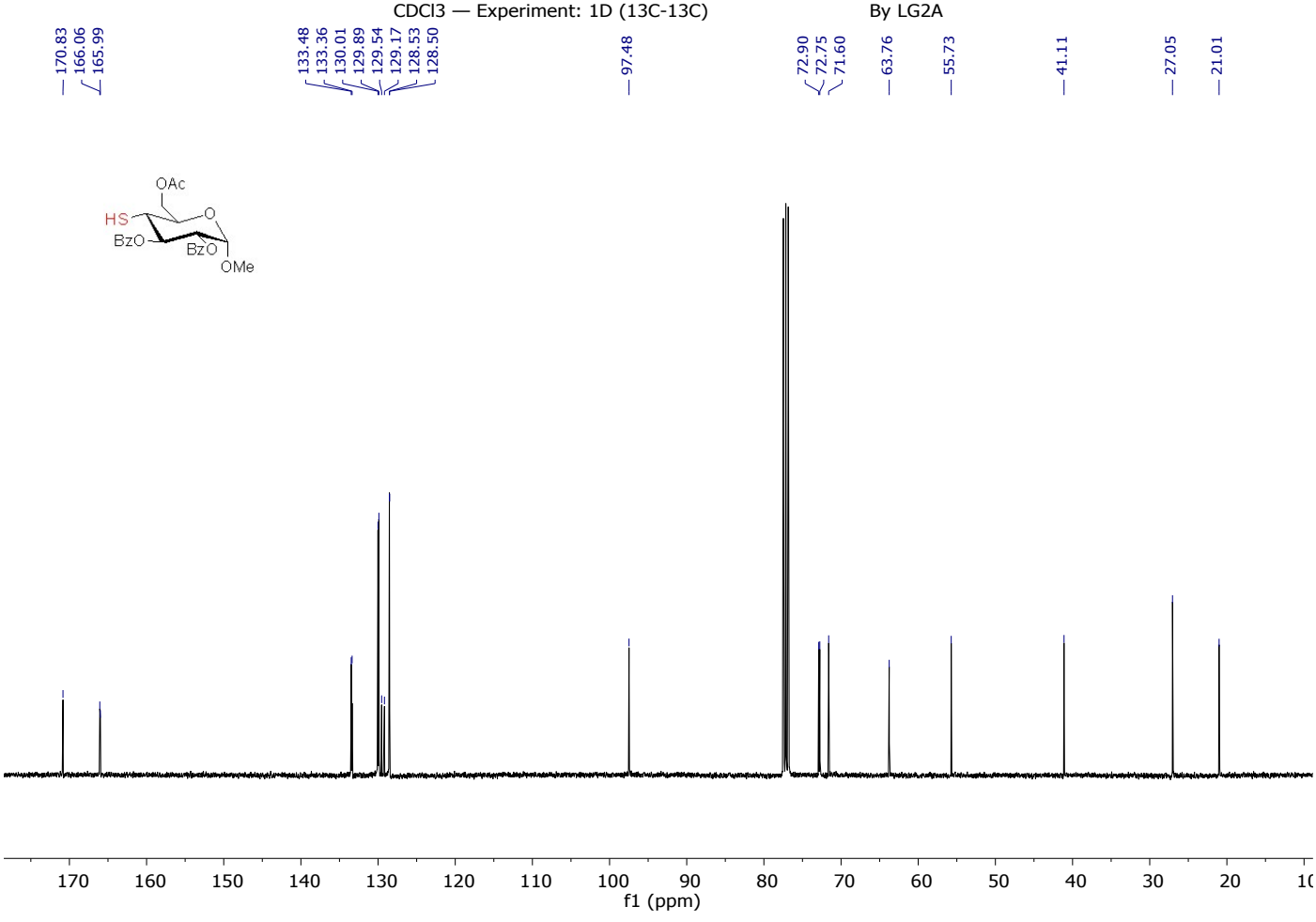
^{1}H (top) and ^{13}C (bottom) NMR spectra of **2**



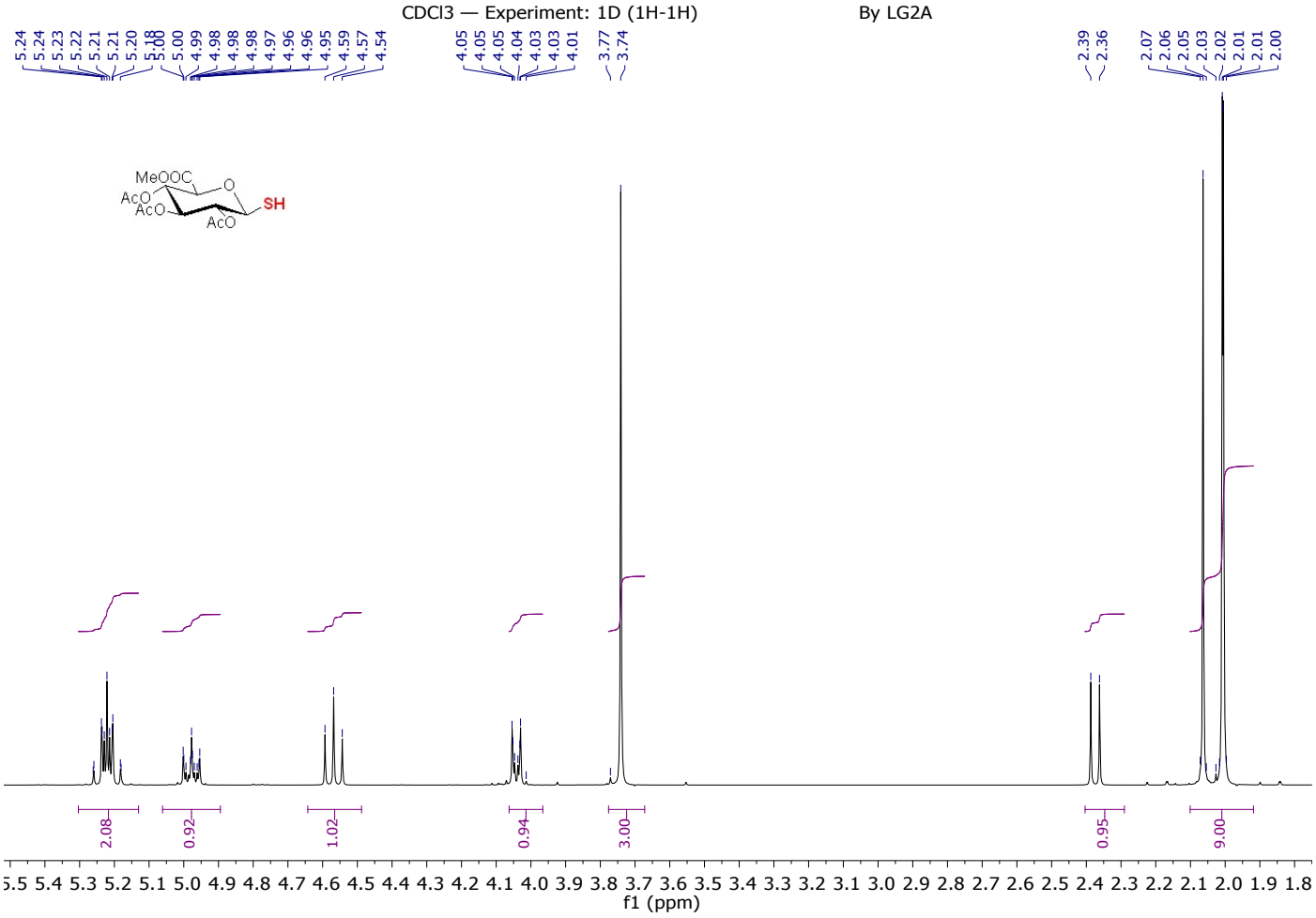


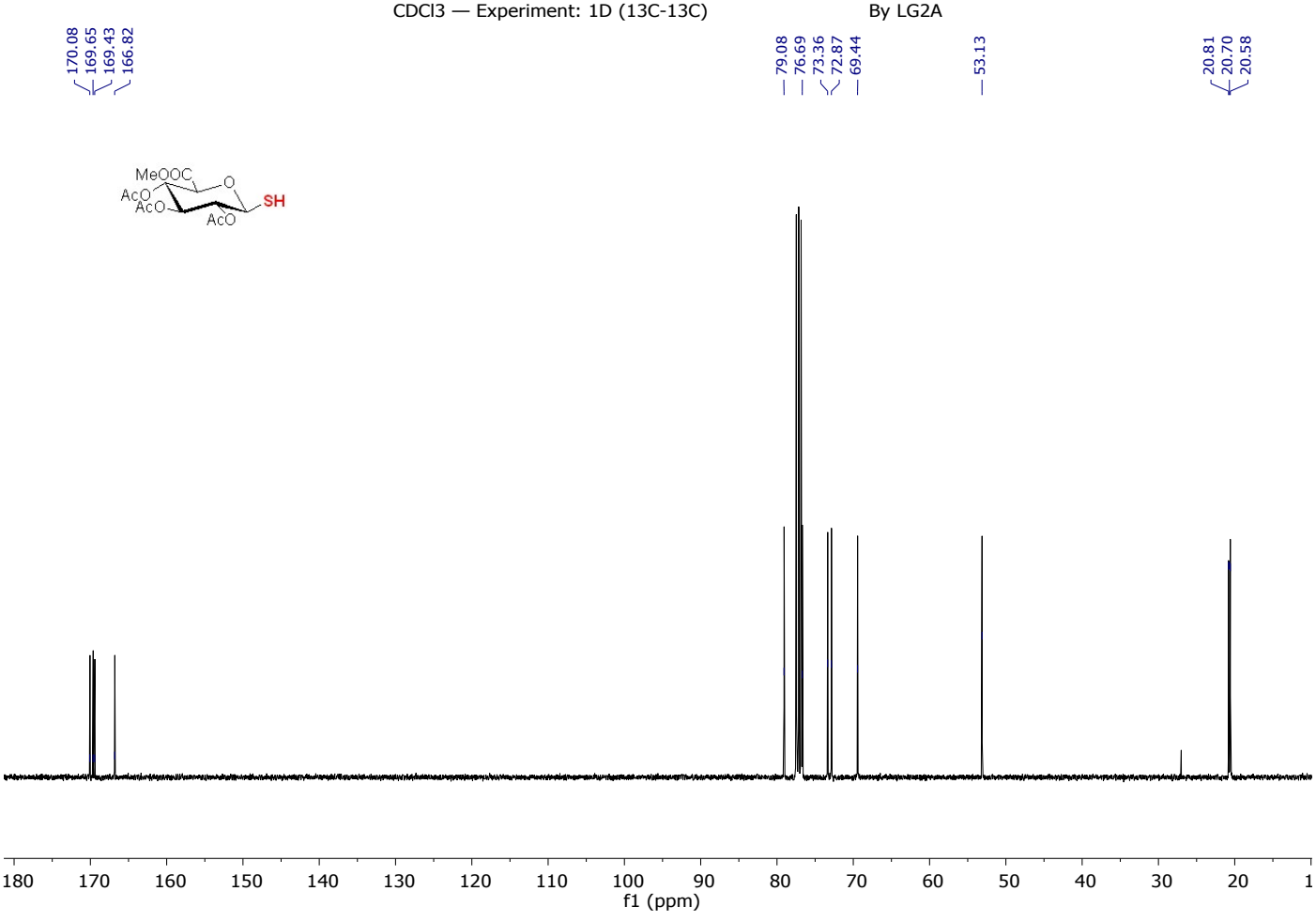
^{1}H (top) and ^{13}C (bottom) NMR spectra of **4**



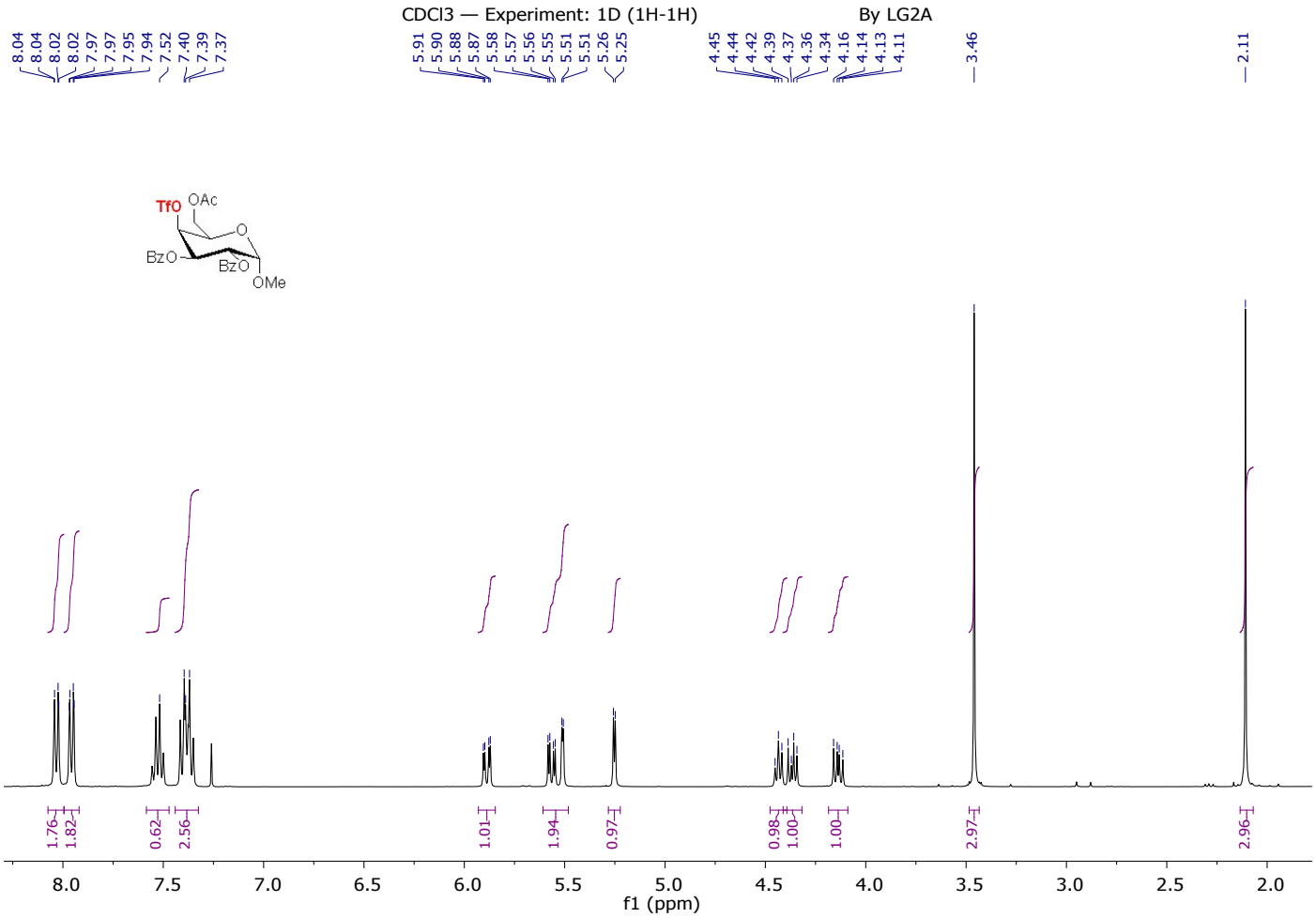


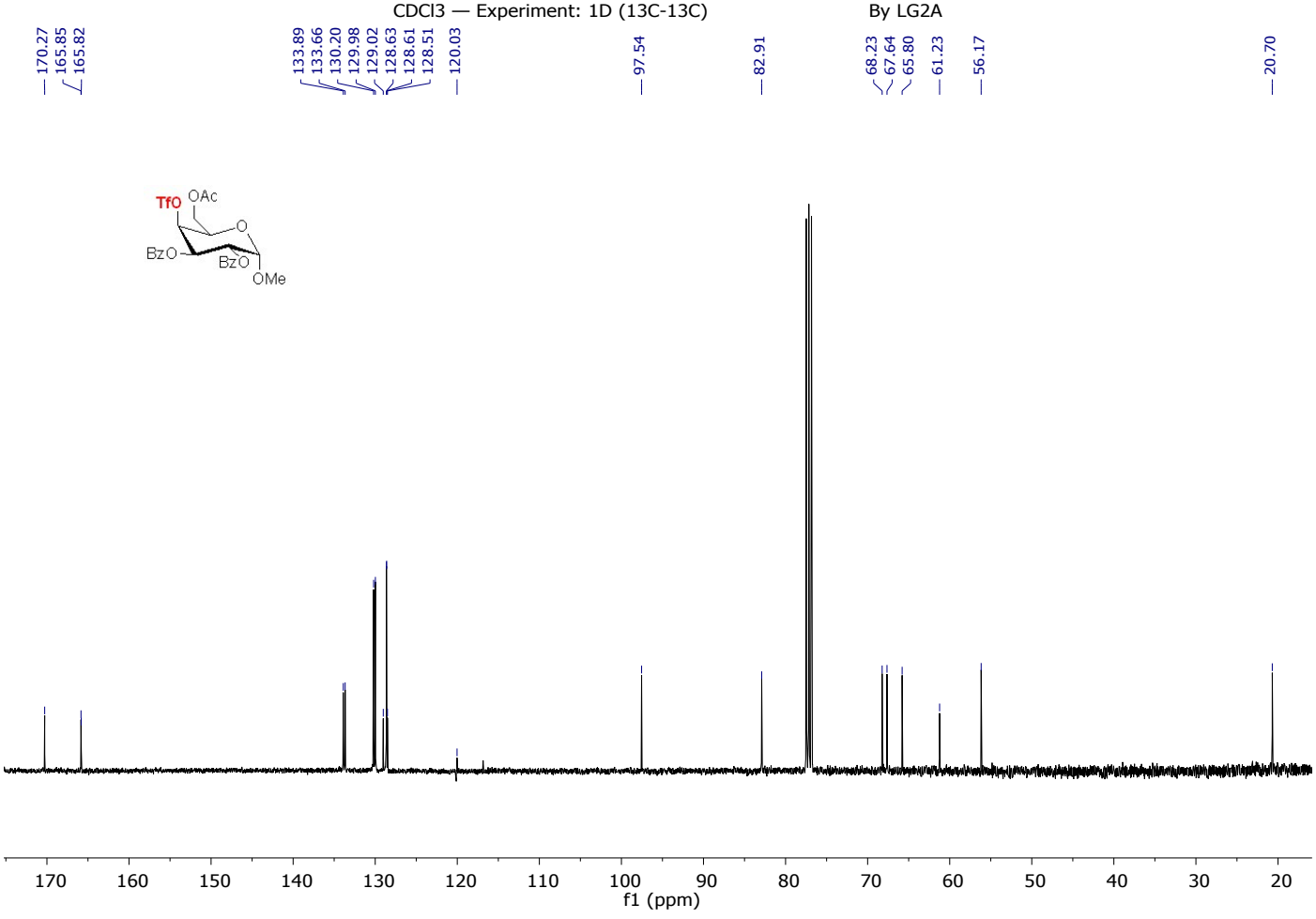
^{1}H (top) and ^{13}C (bottom) NMR spectra of **5**



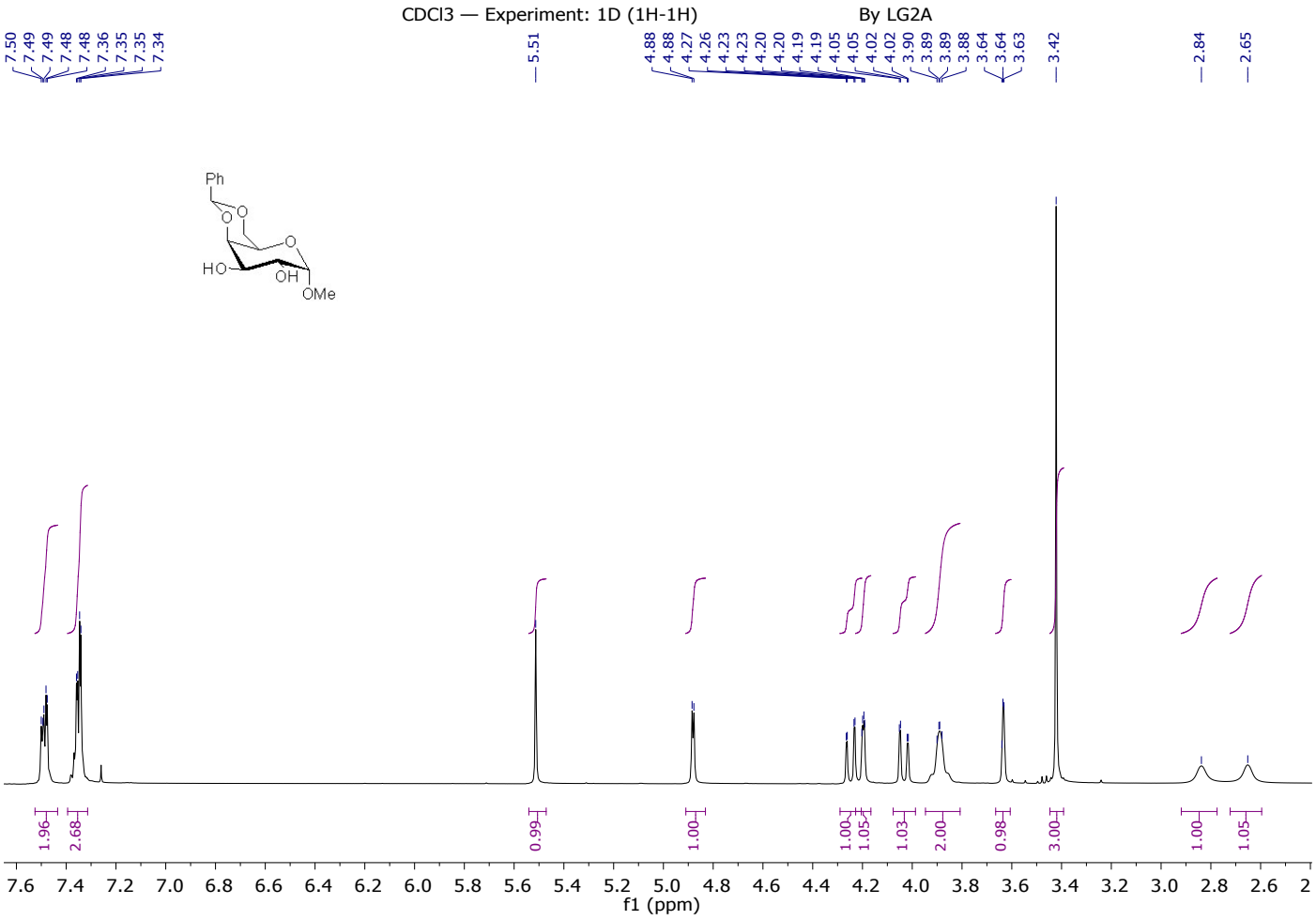


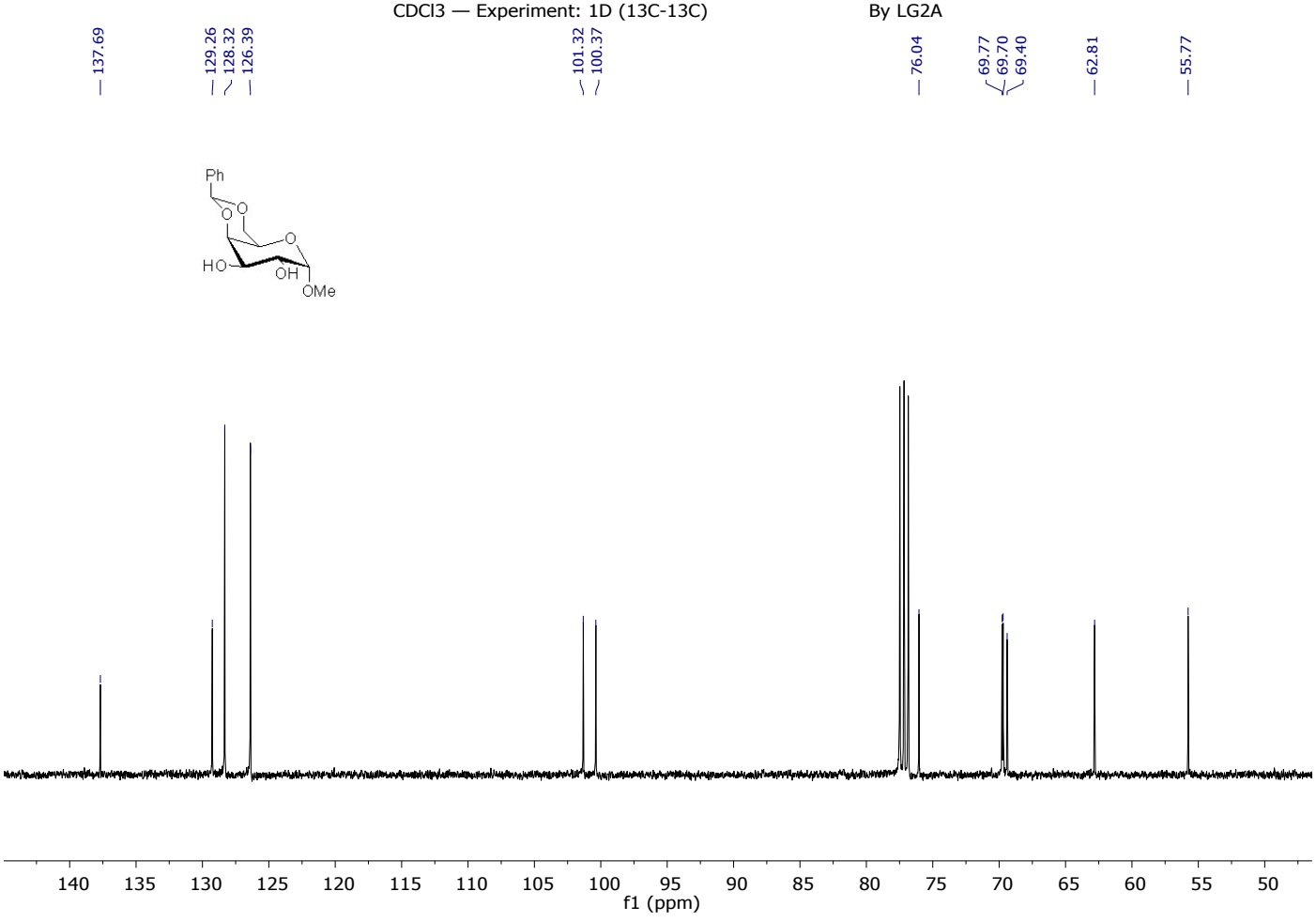
^{1}H (top) and ^{13}C (bottom) NMR spectra of **6**



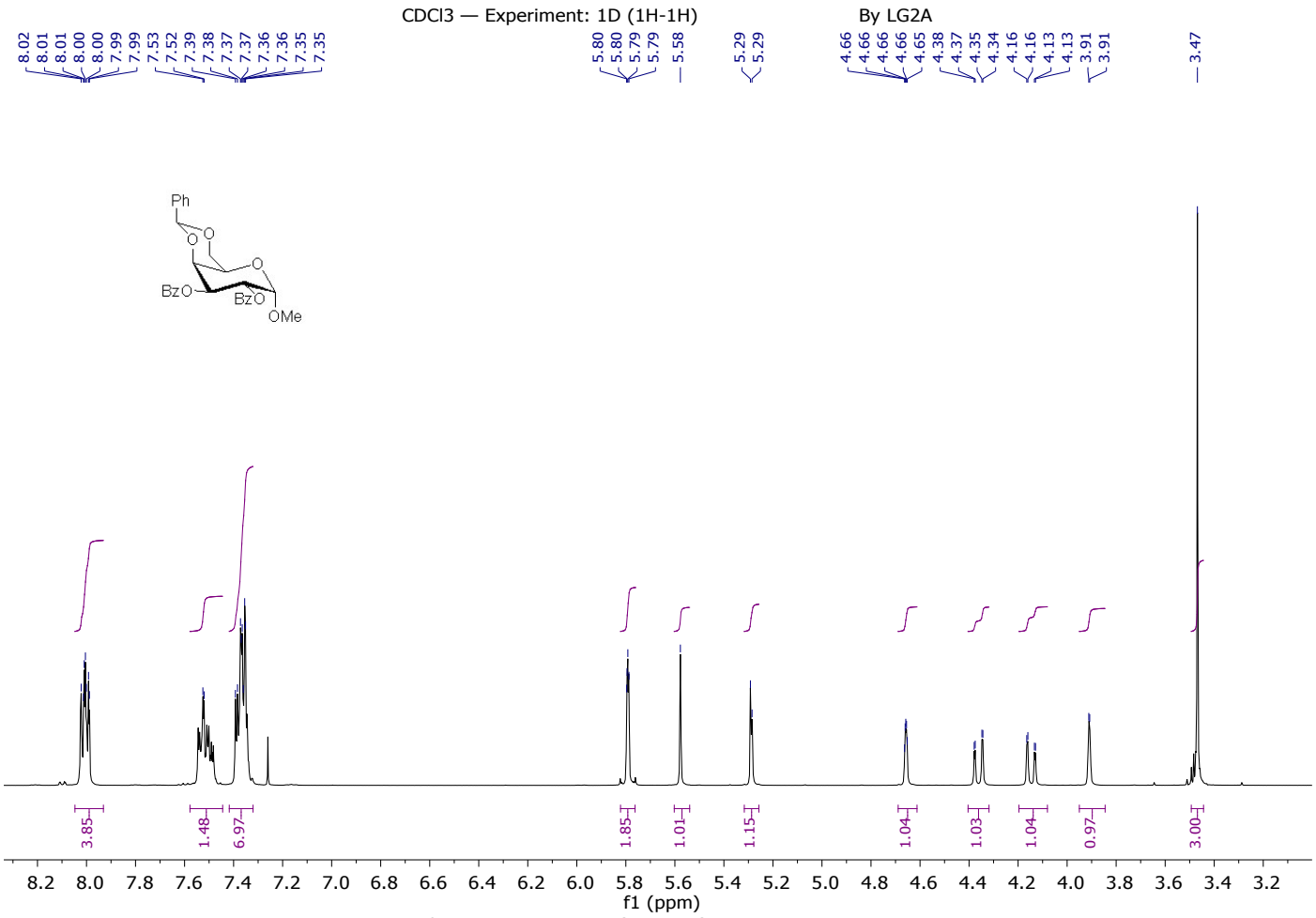


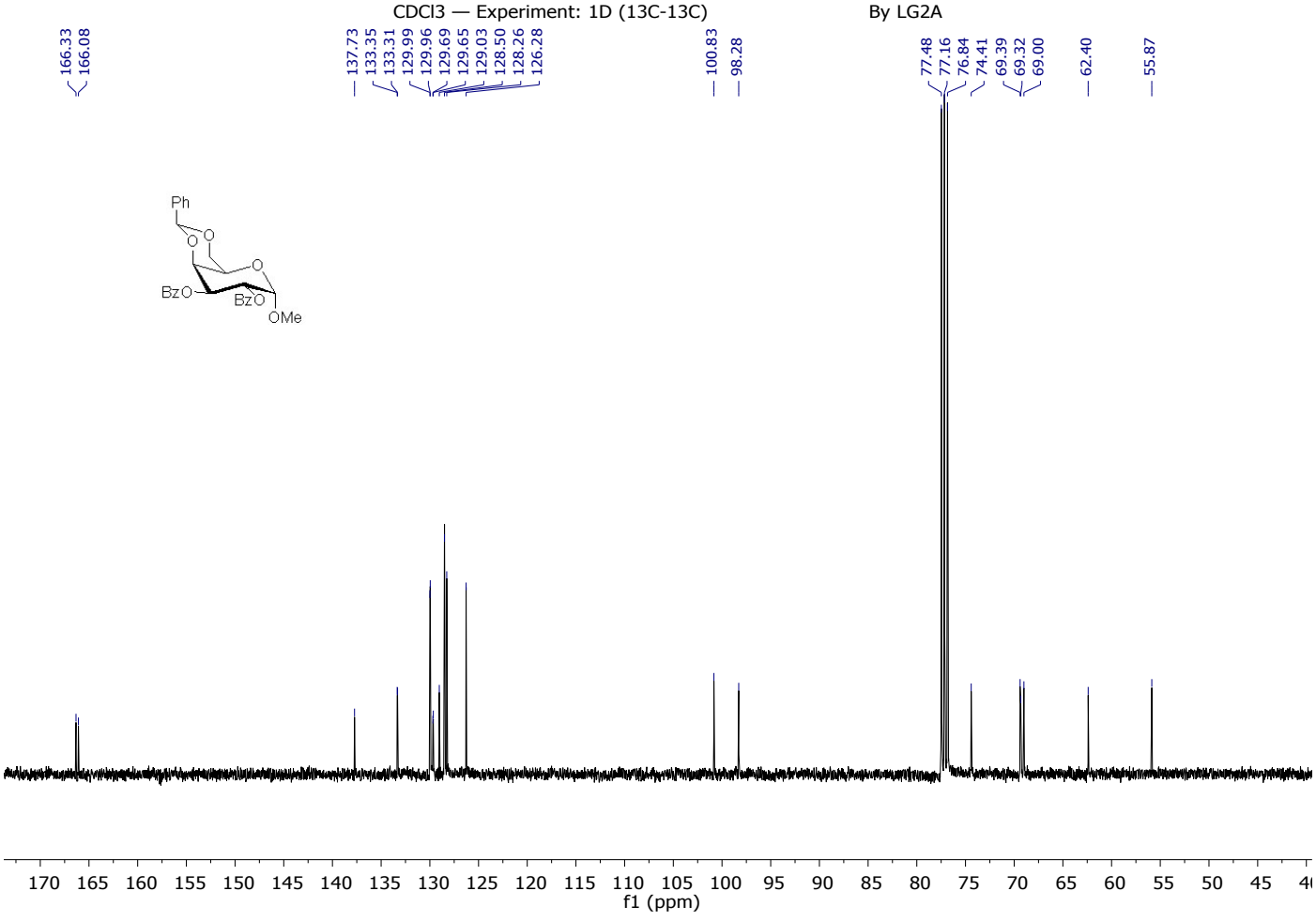
^{1}H (top) and ^{13}C (bottom) NMR spectra of **8**



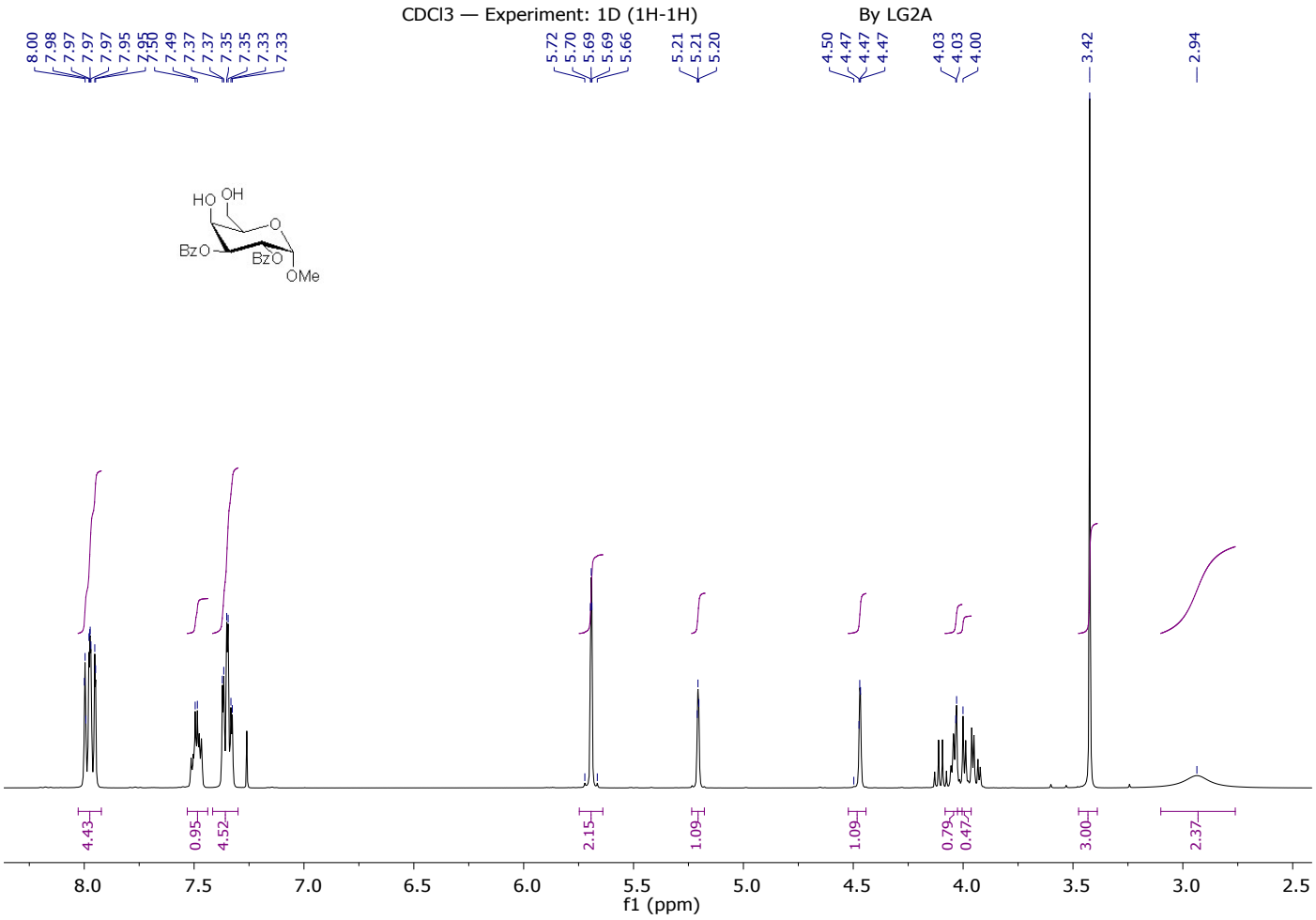


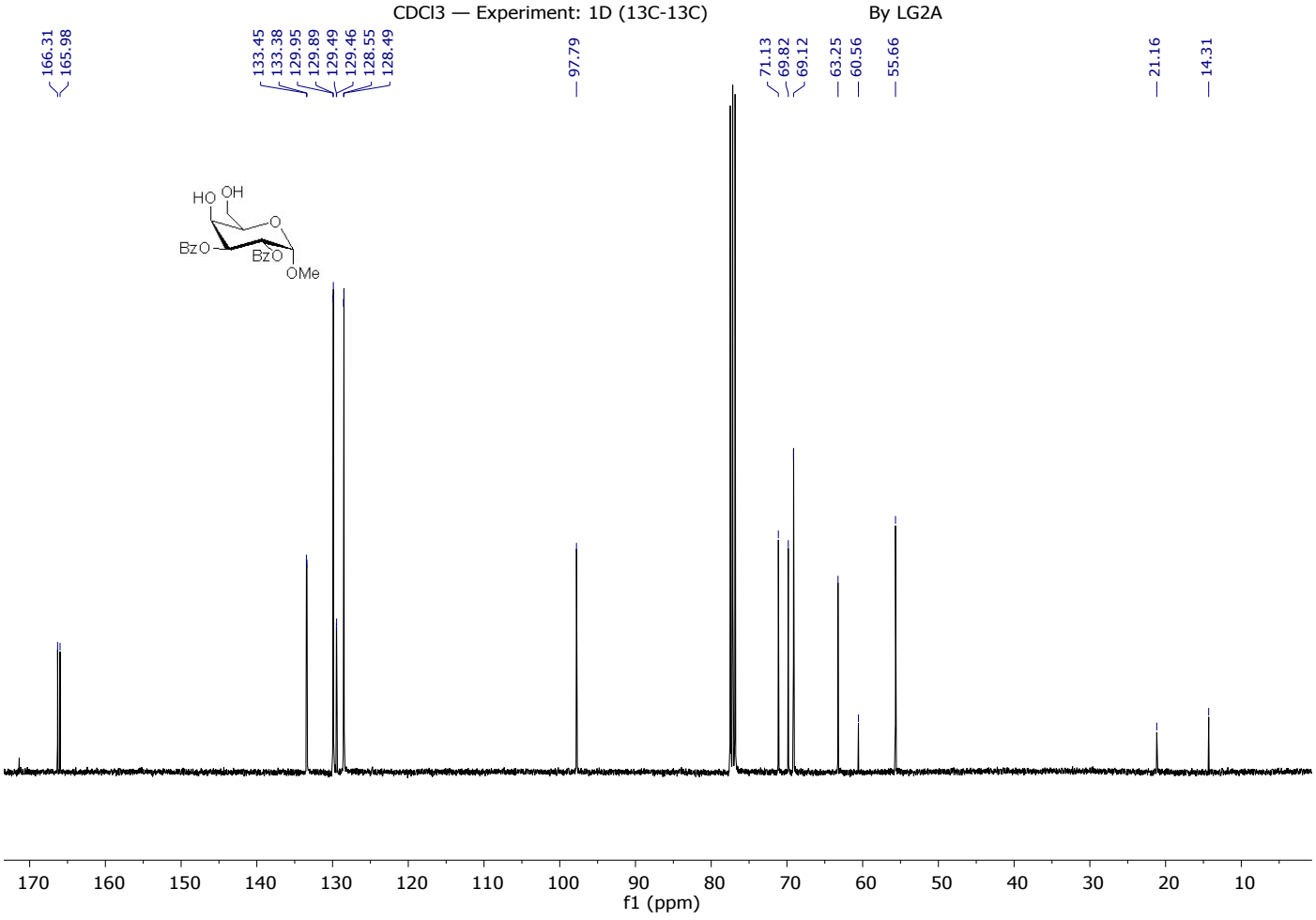
^{1}H (top) and ^{13}C (bottom) NMR spectra of **9**



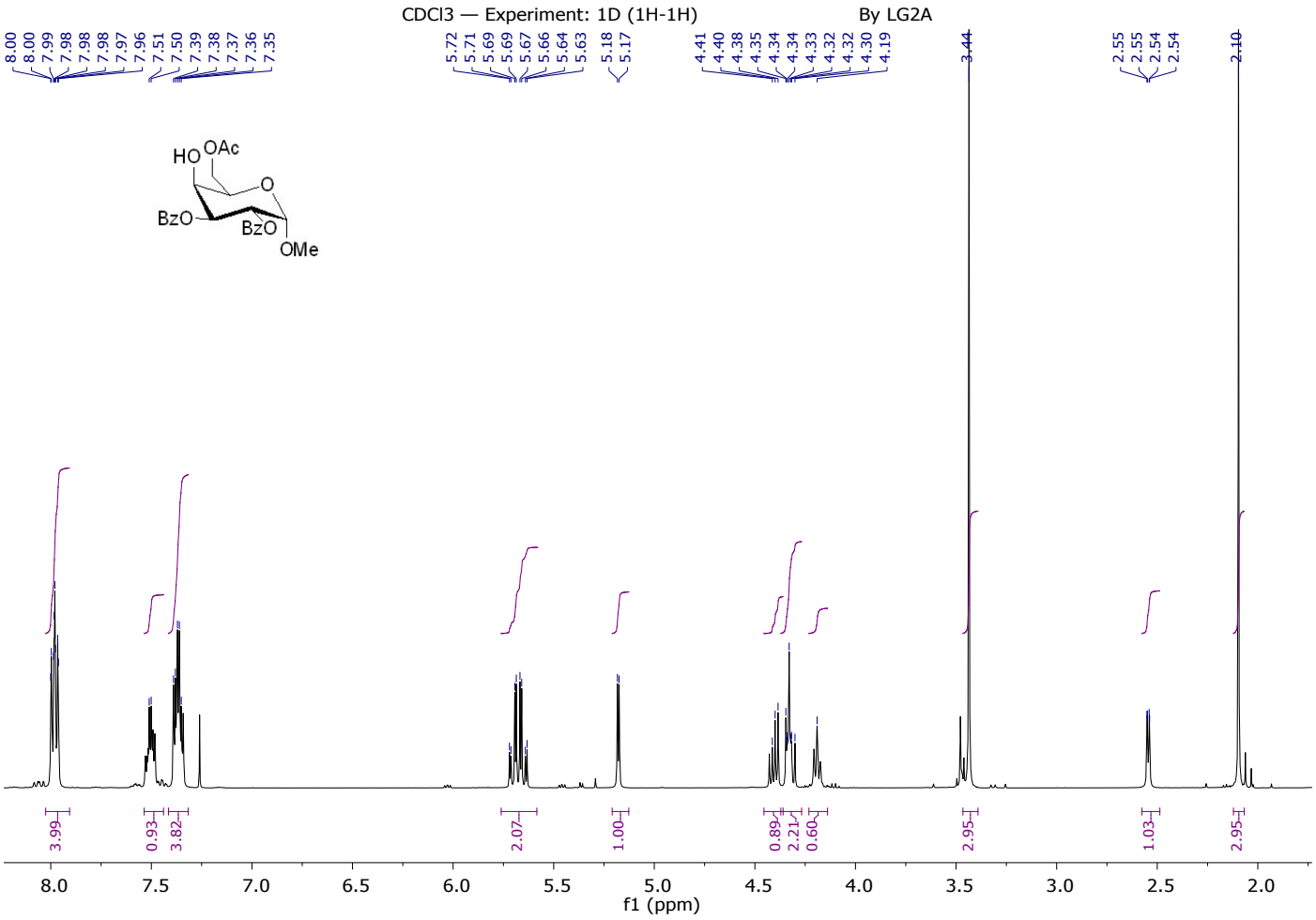


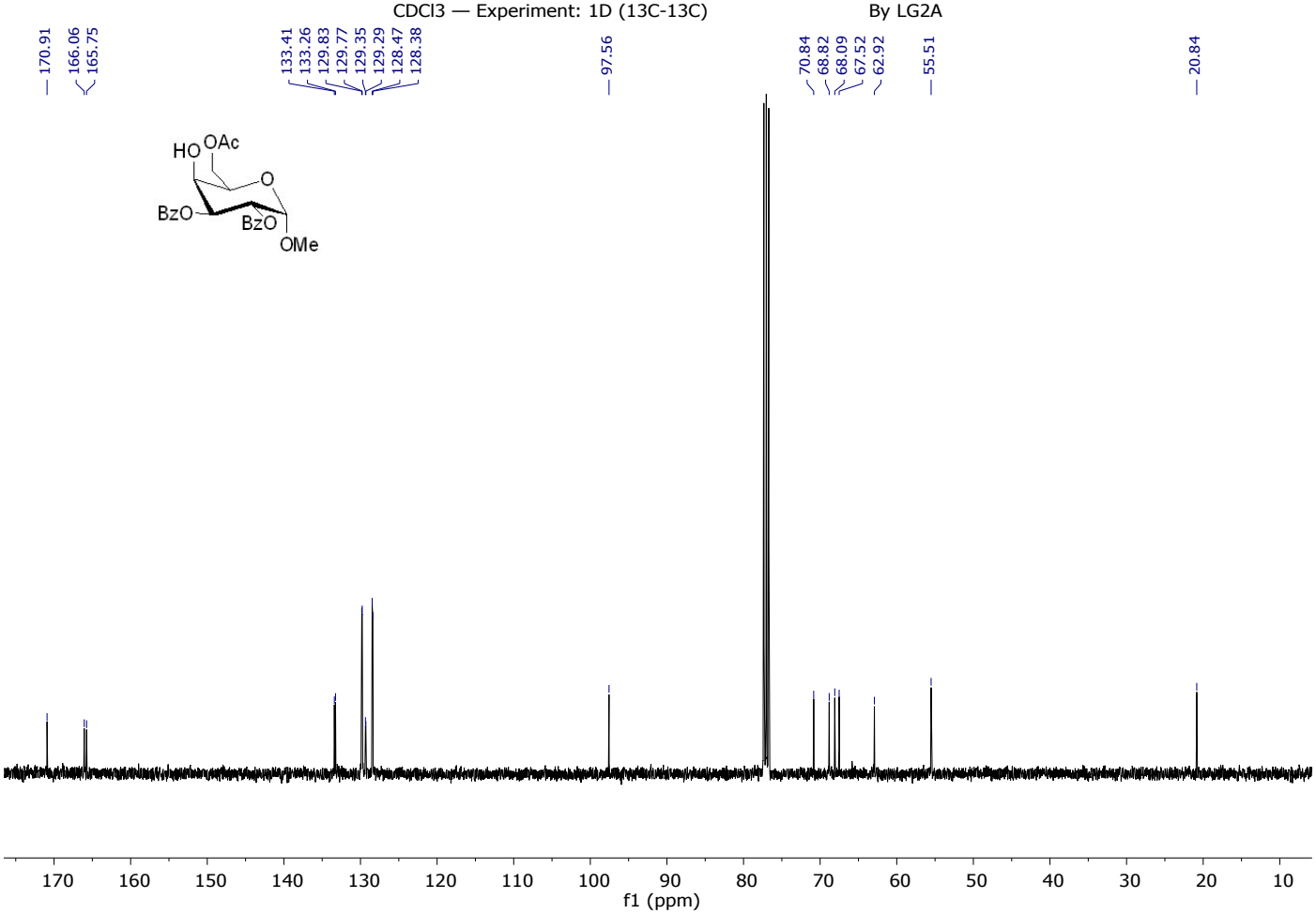
^{1}H (top) and ^{13}C (bottom) NMR spectra of **10**



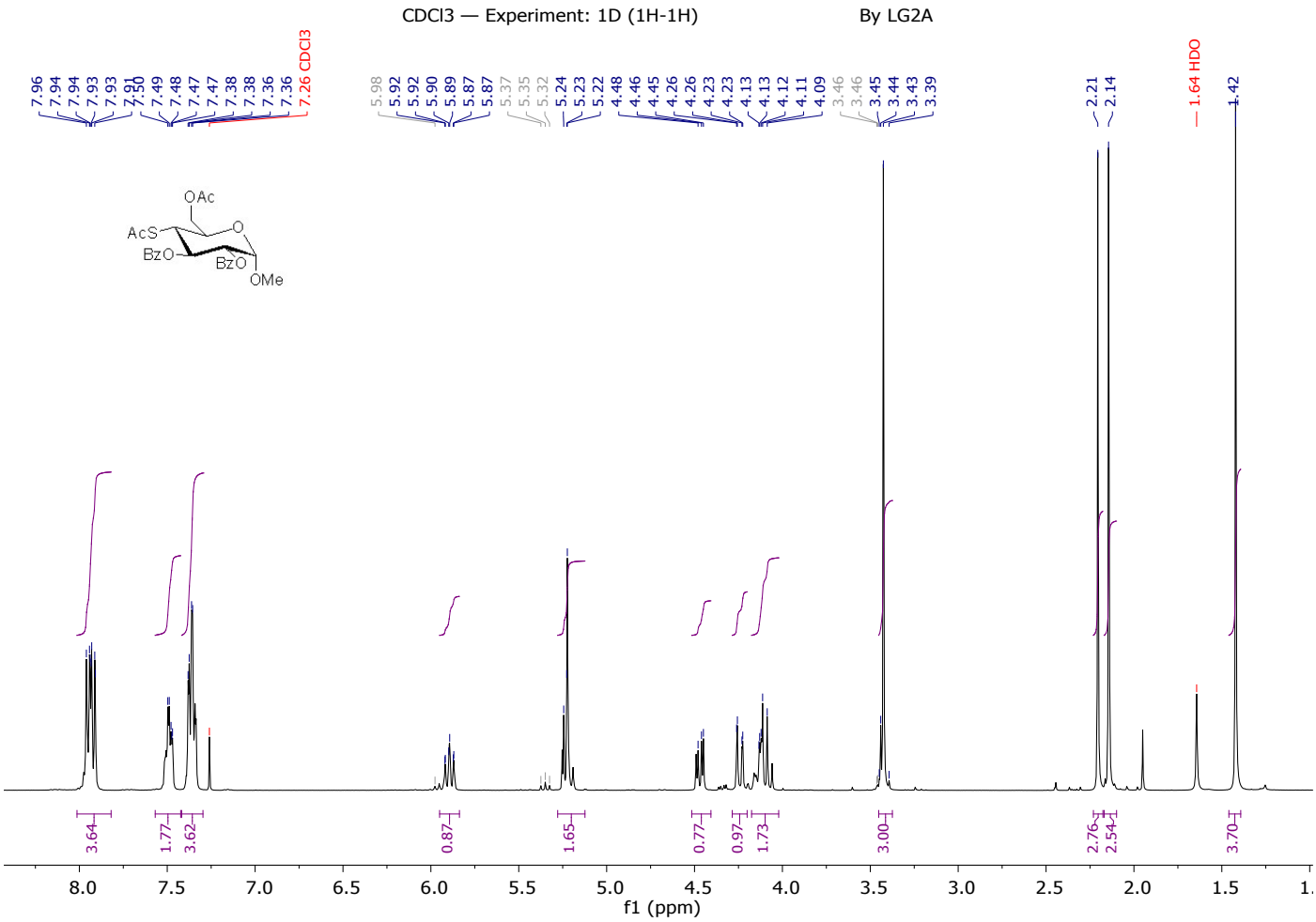


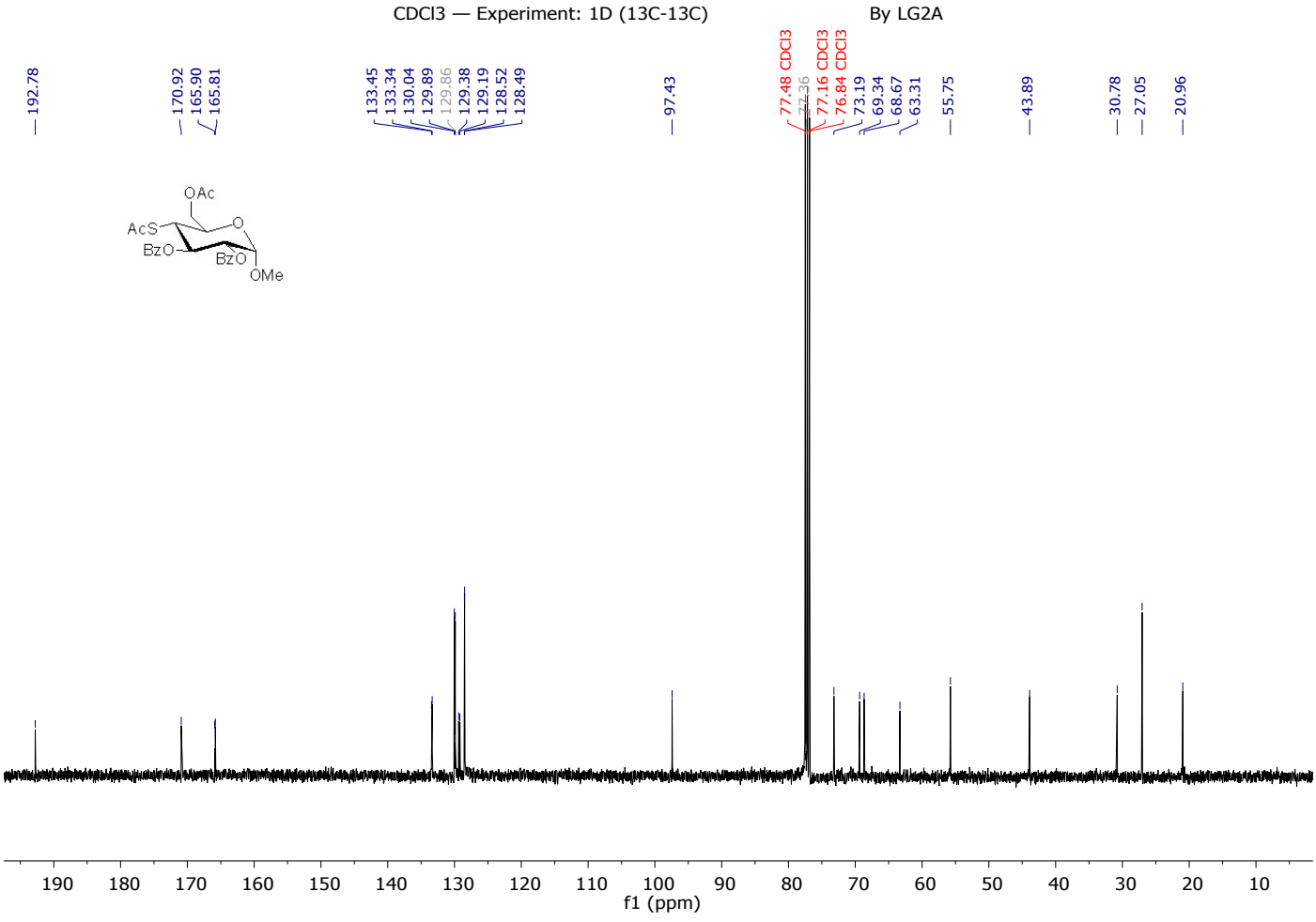
^{1}H (top) and ^{13}C (bottom) NMR spectra of **11**



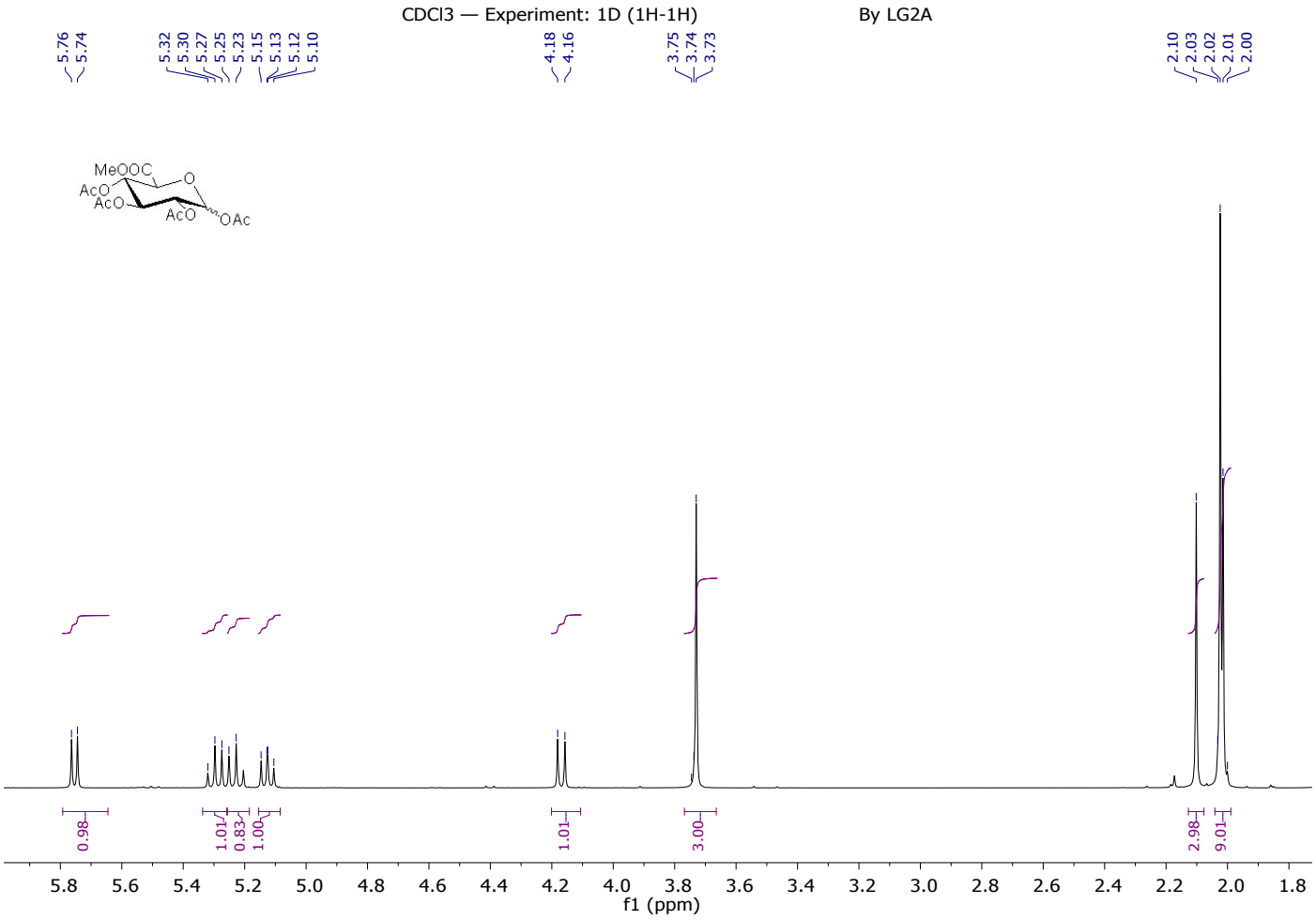


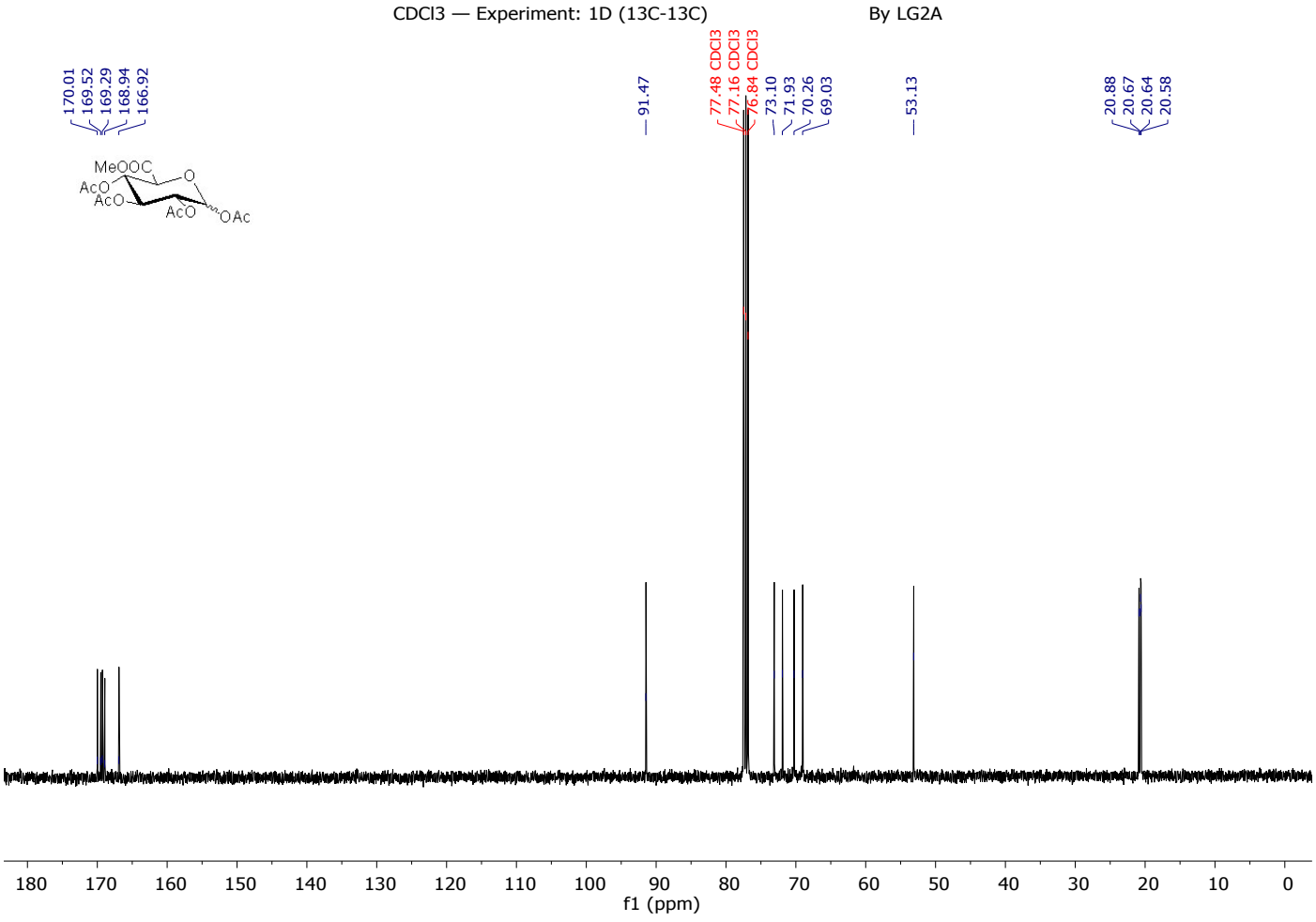
^{1}H (top) and ^{13}C (bottom) NMR spectra of **12**



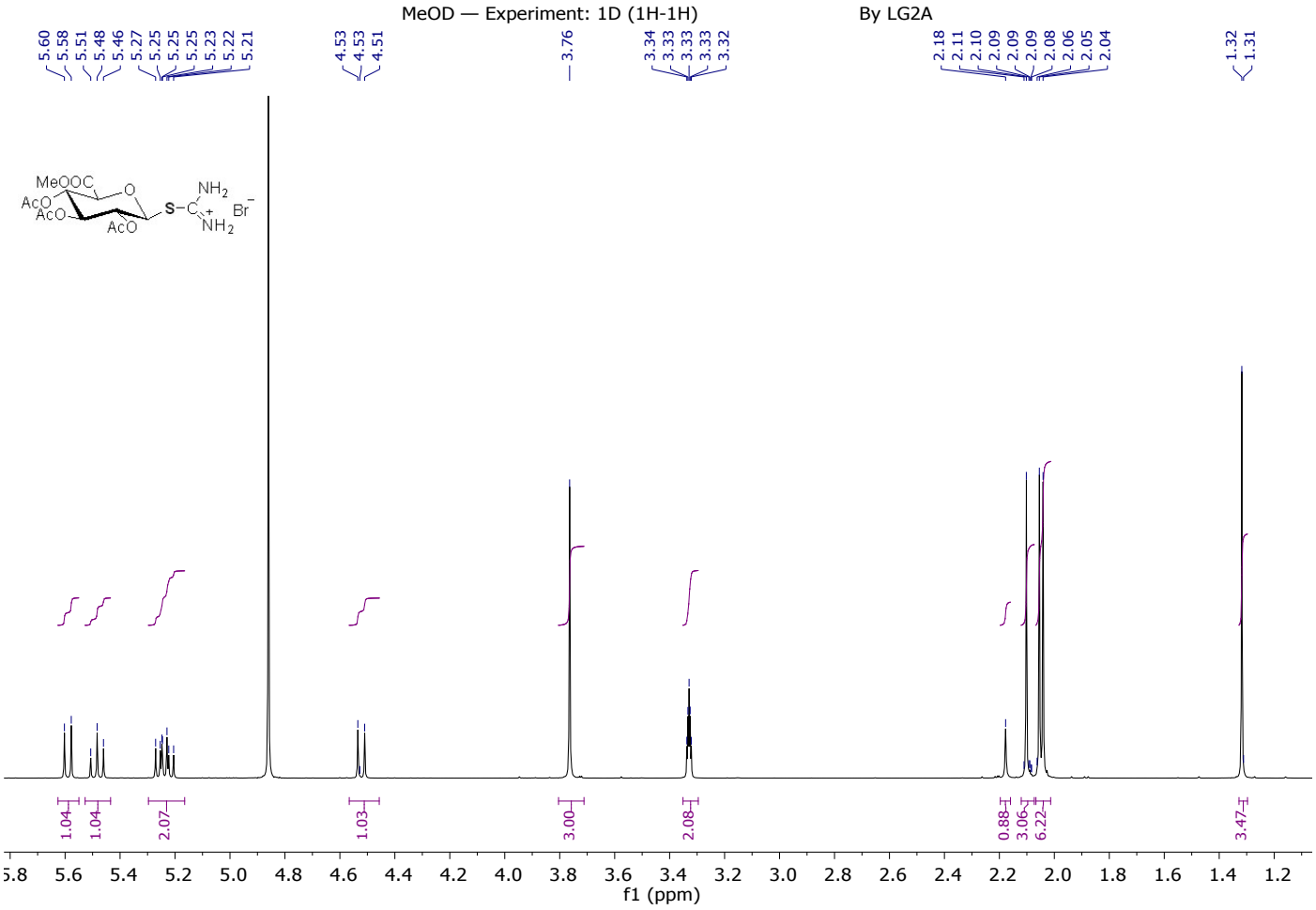


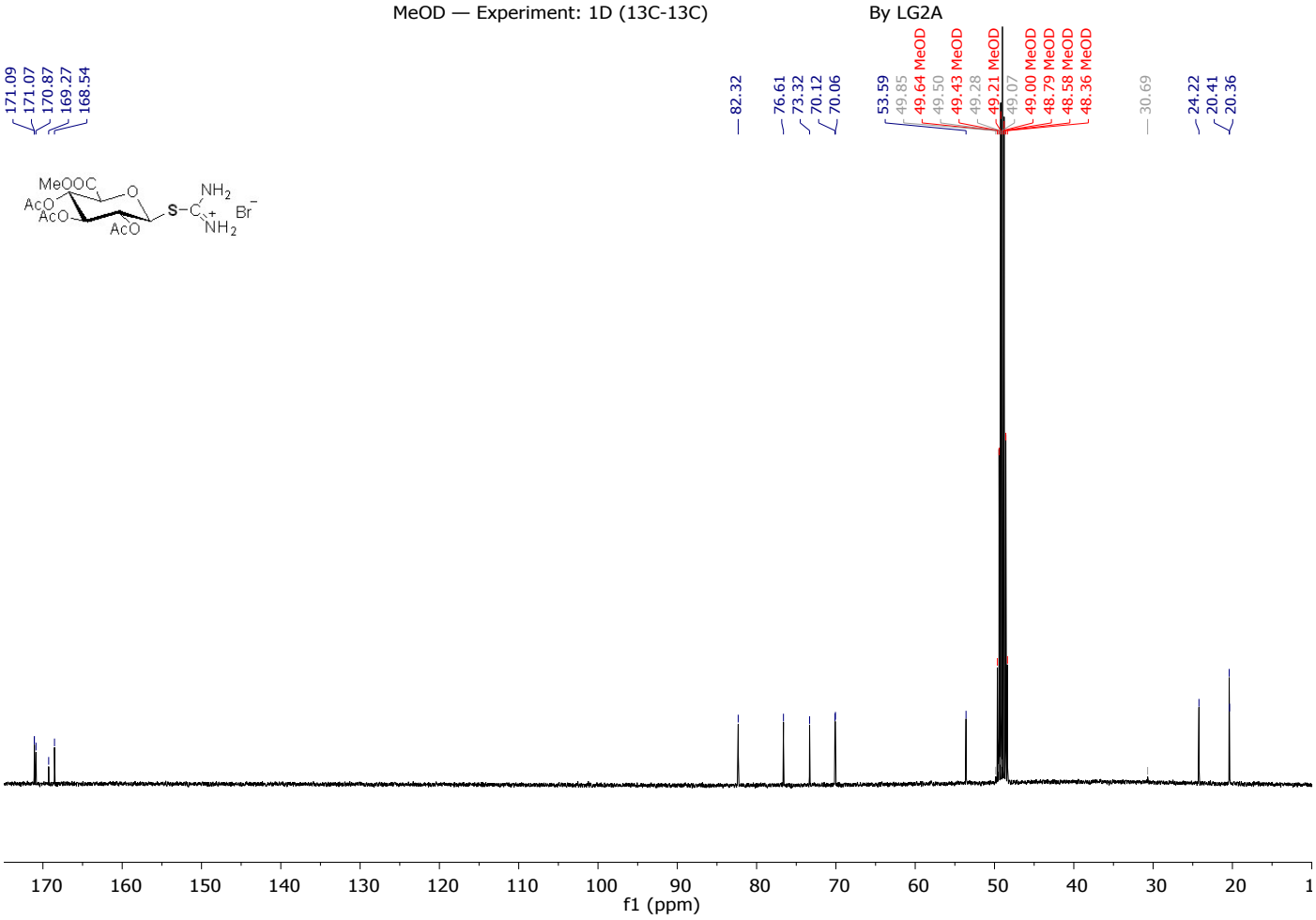
^{1}H (top) and ^{13}C (bottom) NMR spectra of **14**



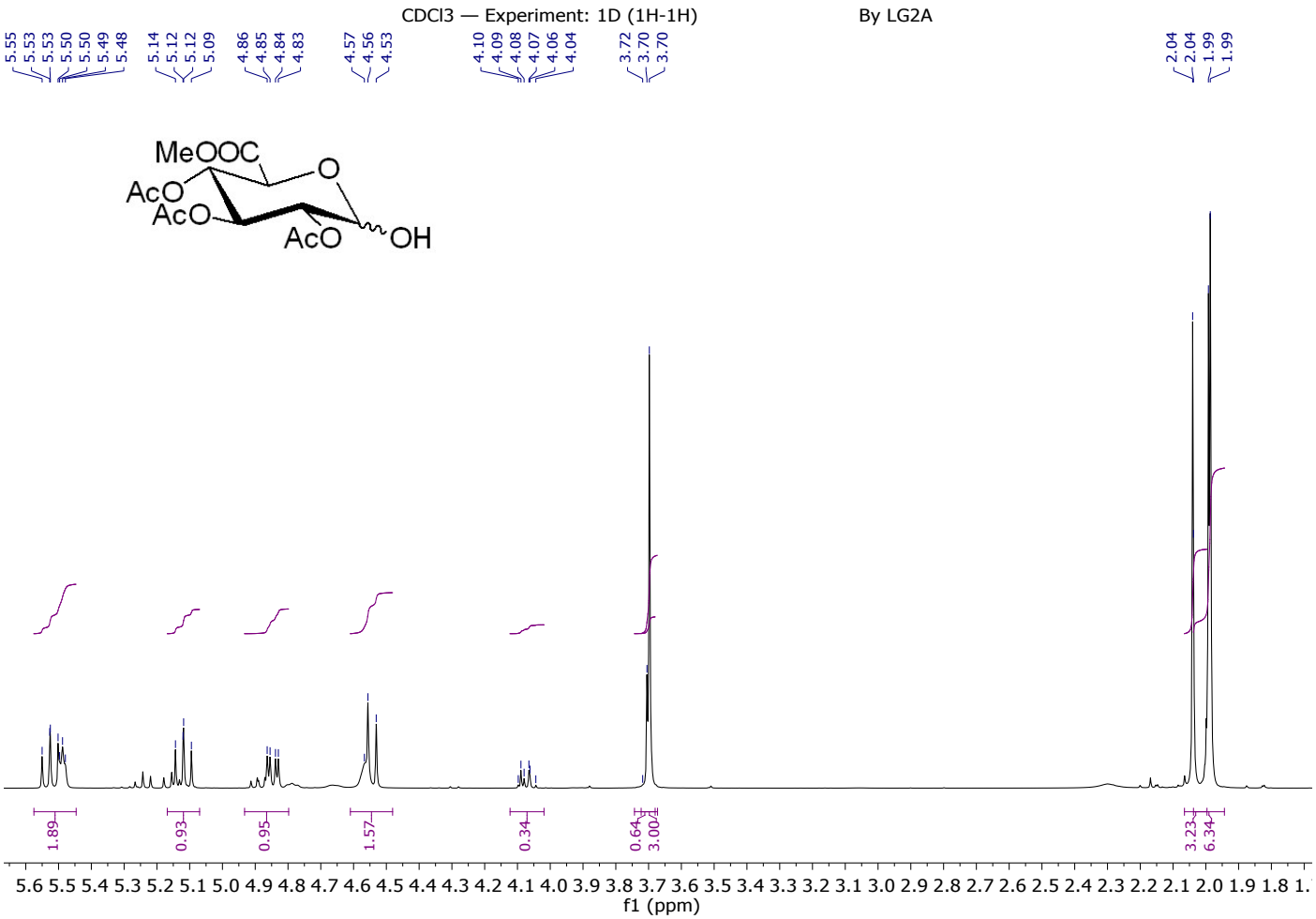


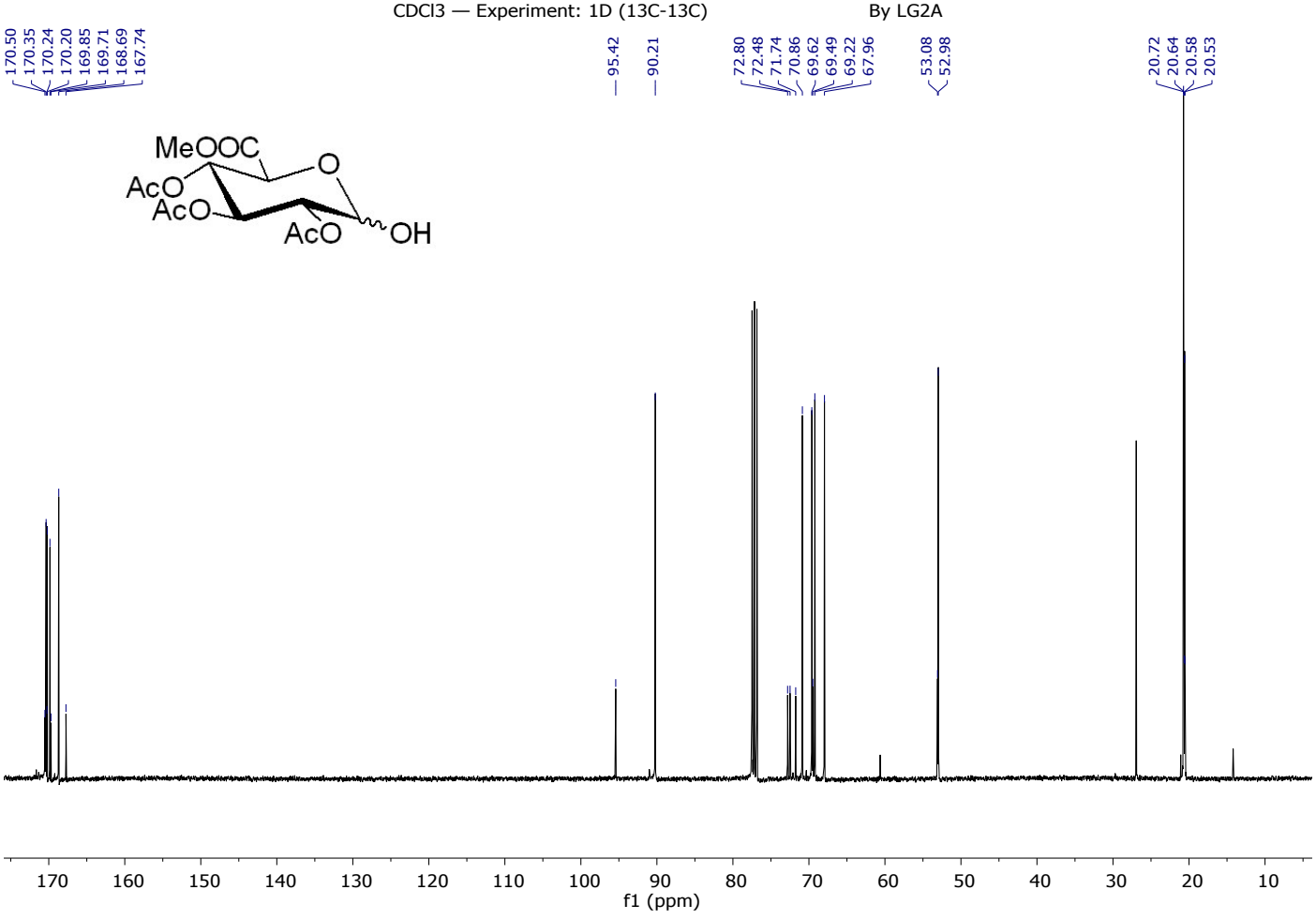
^{1}H (top) and ^{13}C (bottom) NMR spectra of **15**



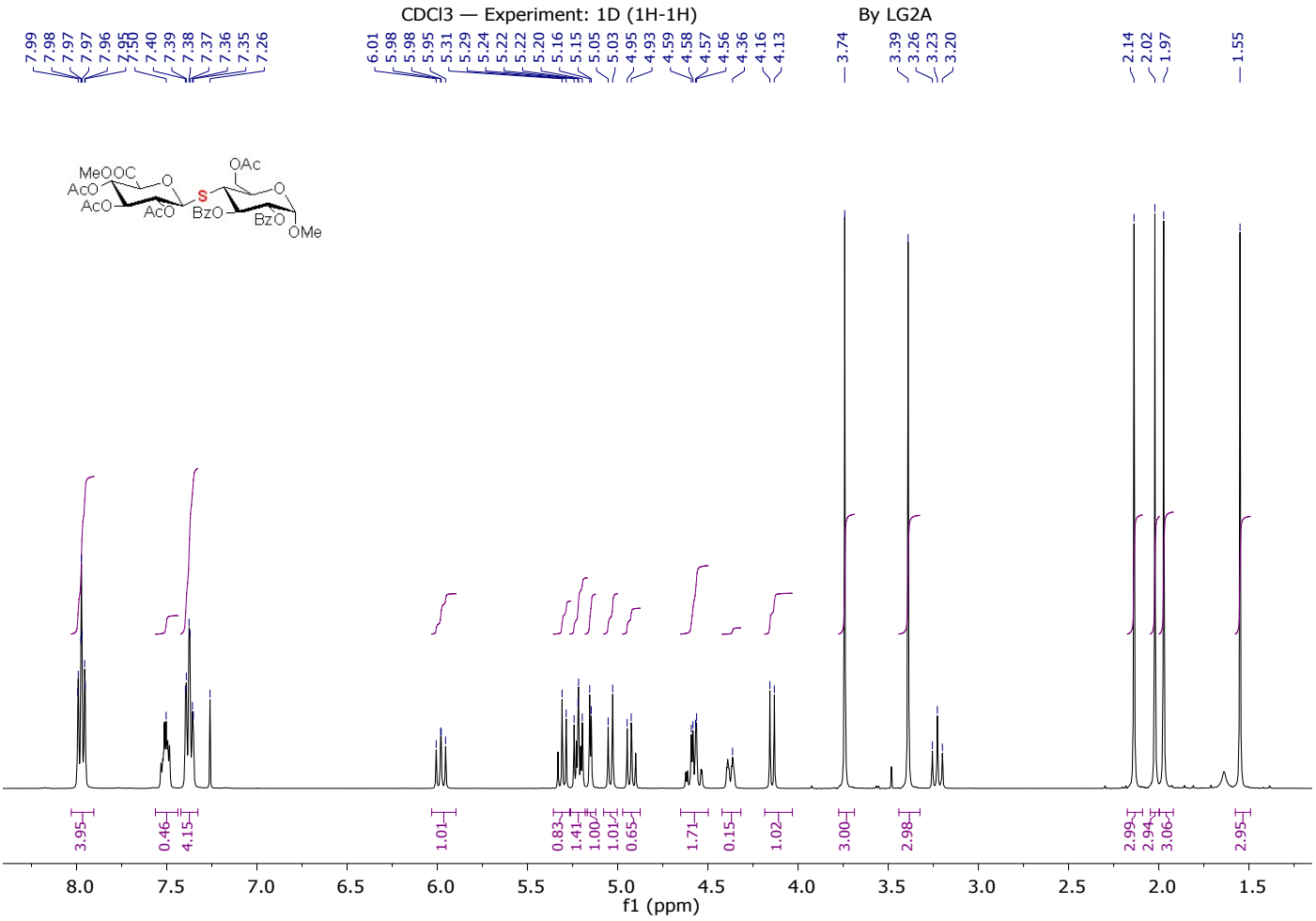


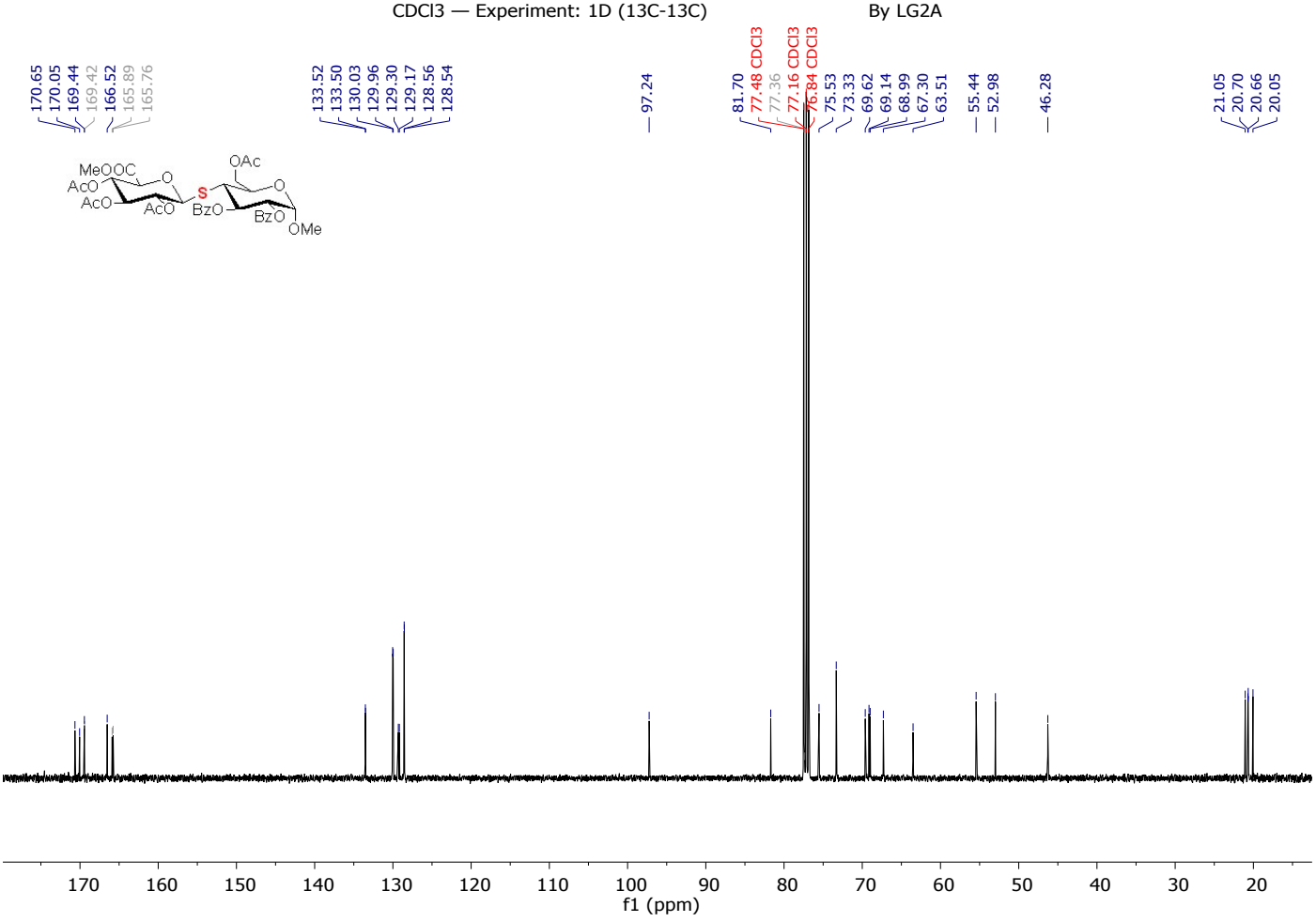
^{1}H (top) and ^{13}C (bottom) NMR spectra of **16**



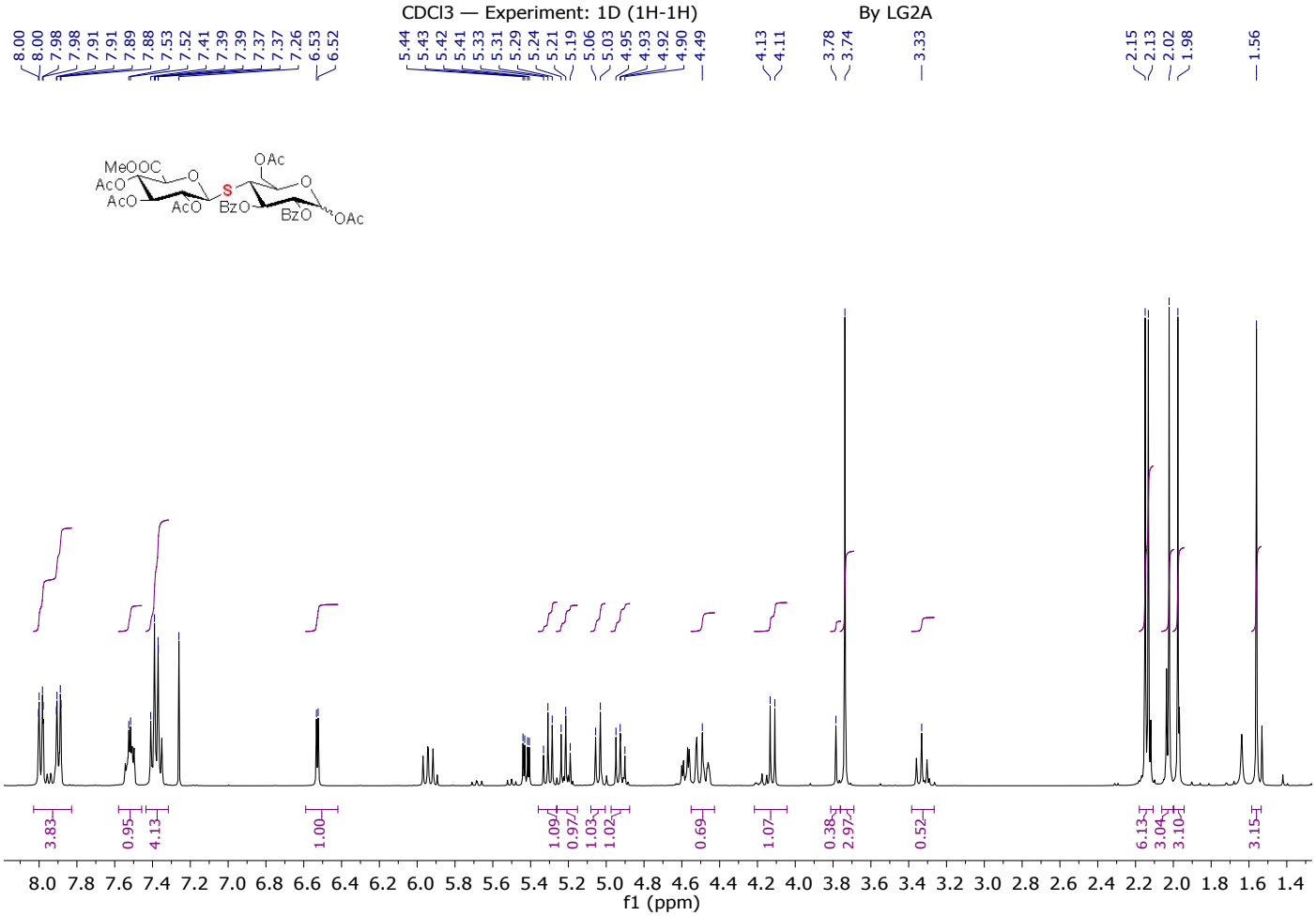


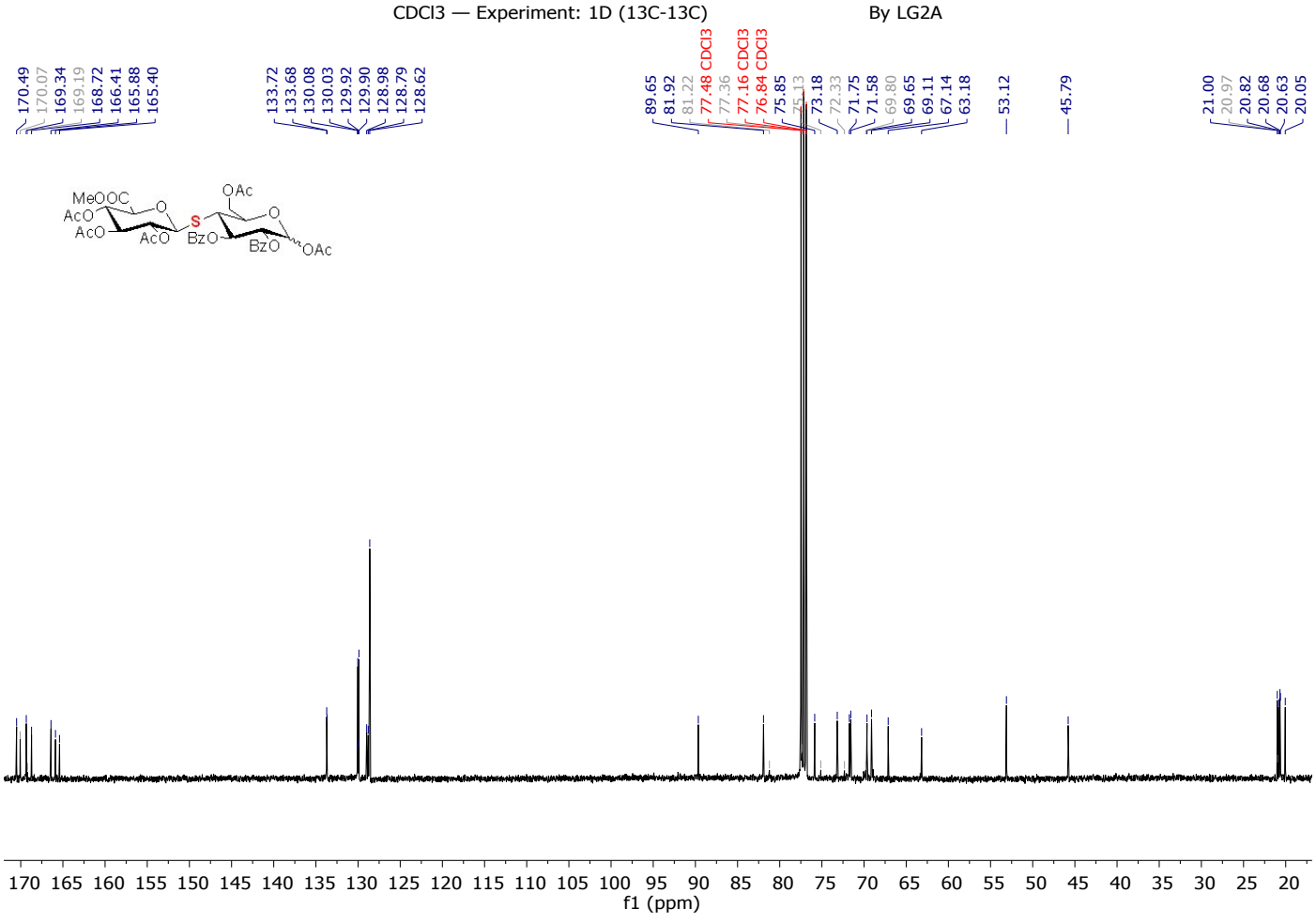
^{1}H (top) and ^{13}C (bottom) NMR spectra of **17β**



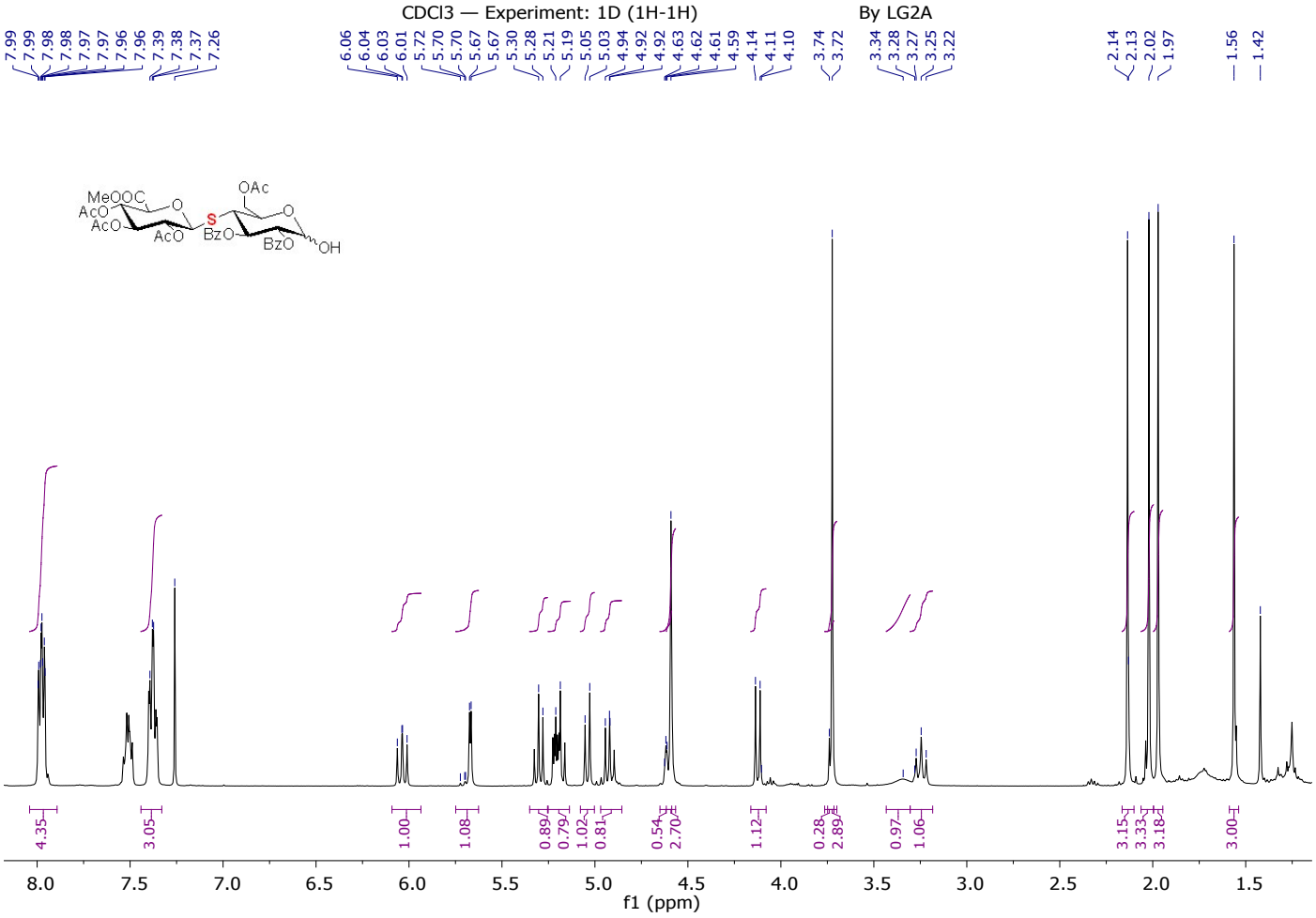


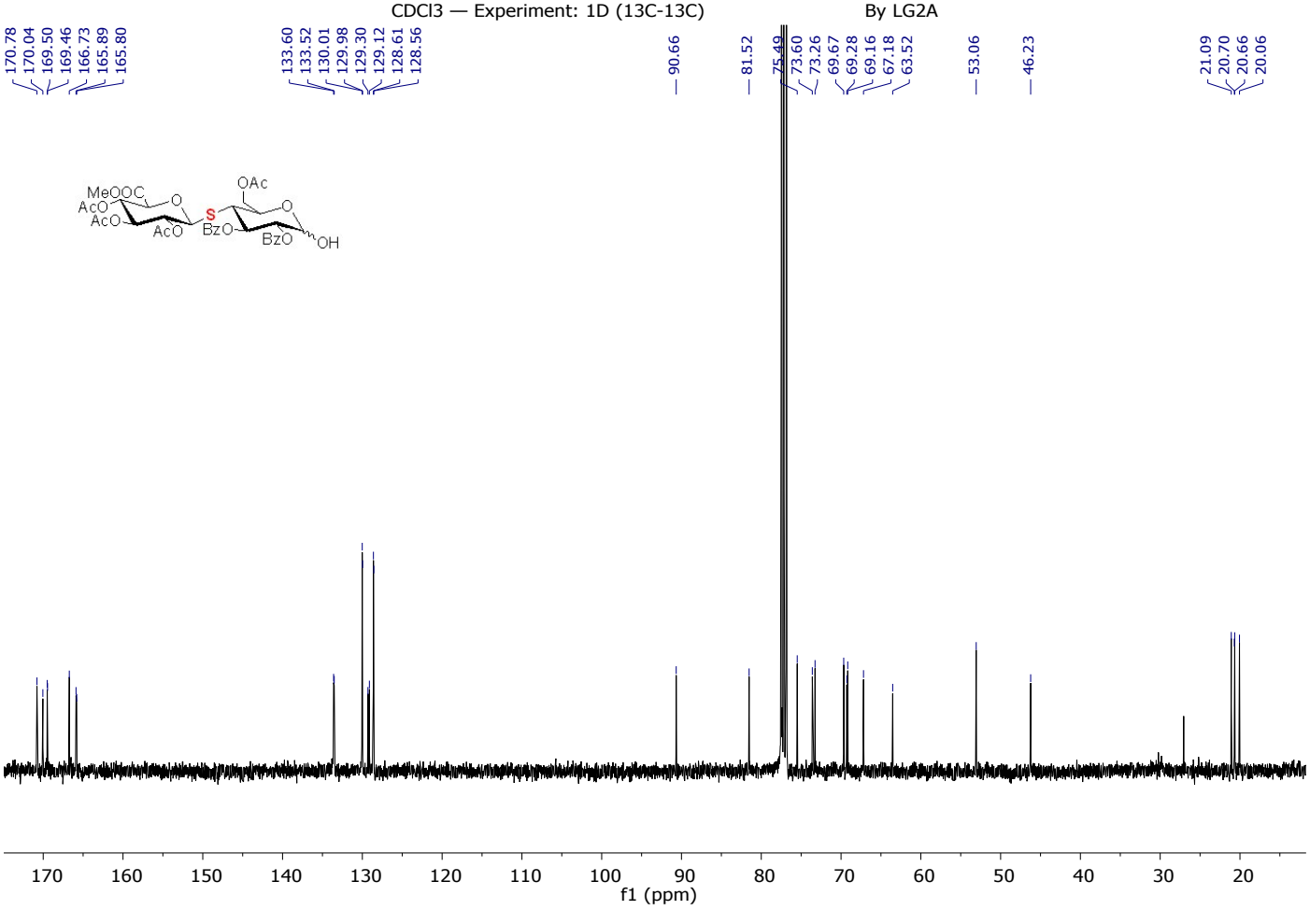
^{1}H (top) and ^{13}C (bottom) NMR spectra of **18**



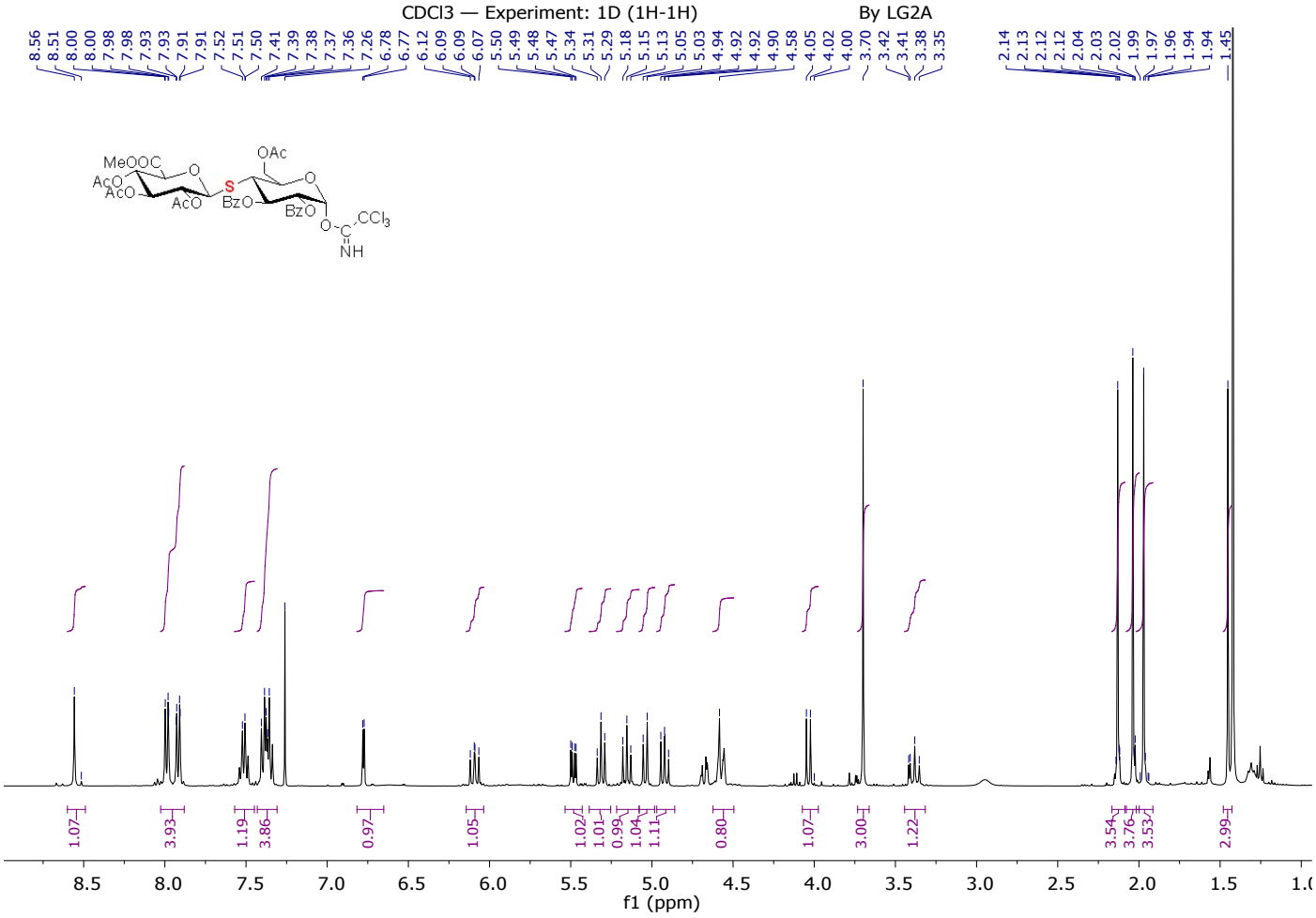


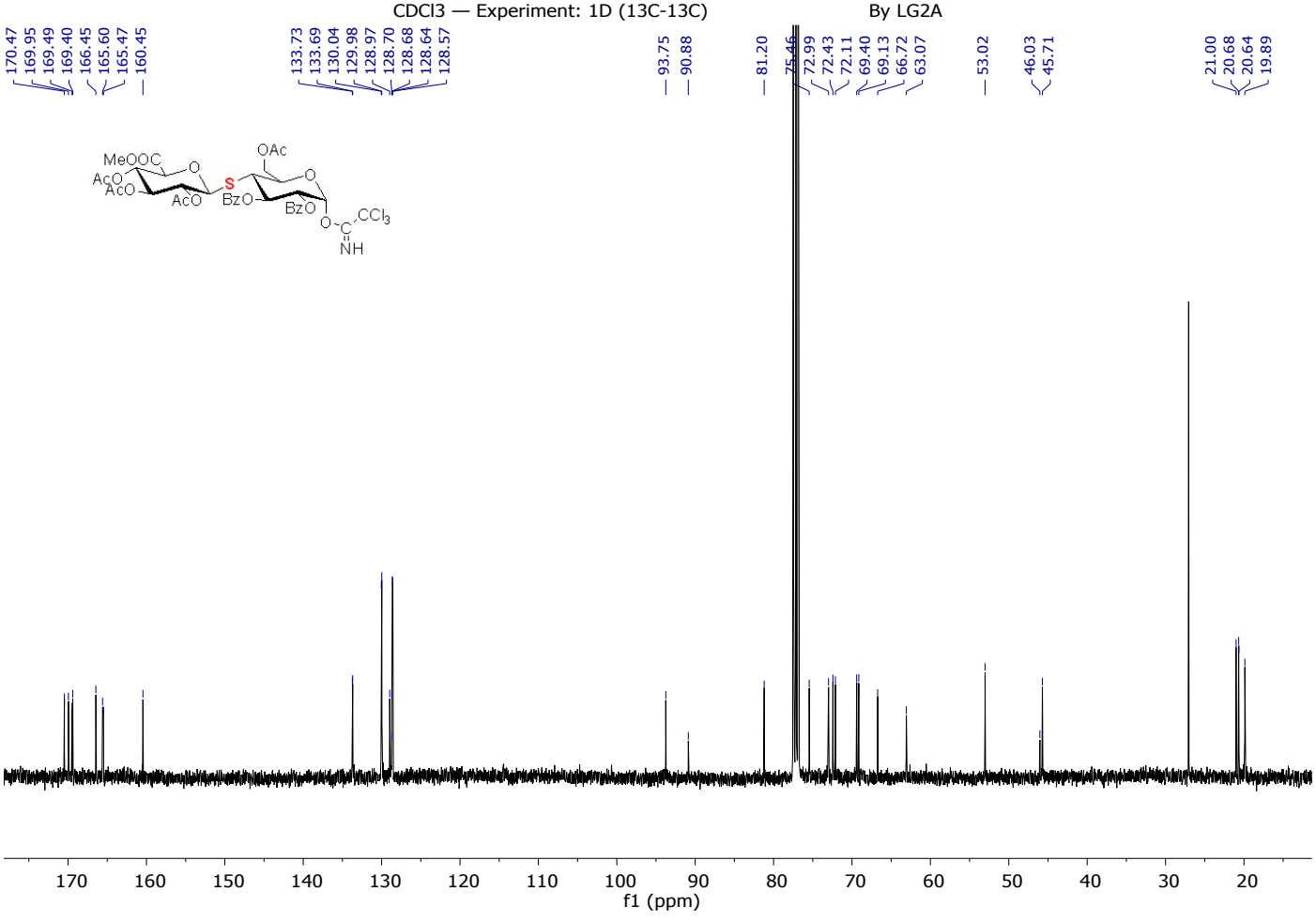
^{1}H (top) and ^{13}C (bottom) NMR spectra of **19**



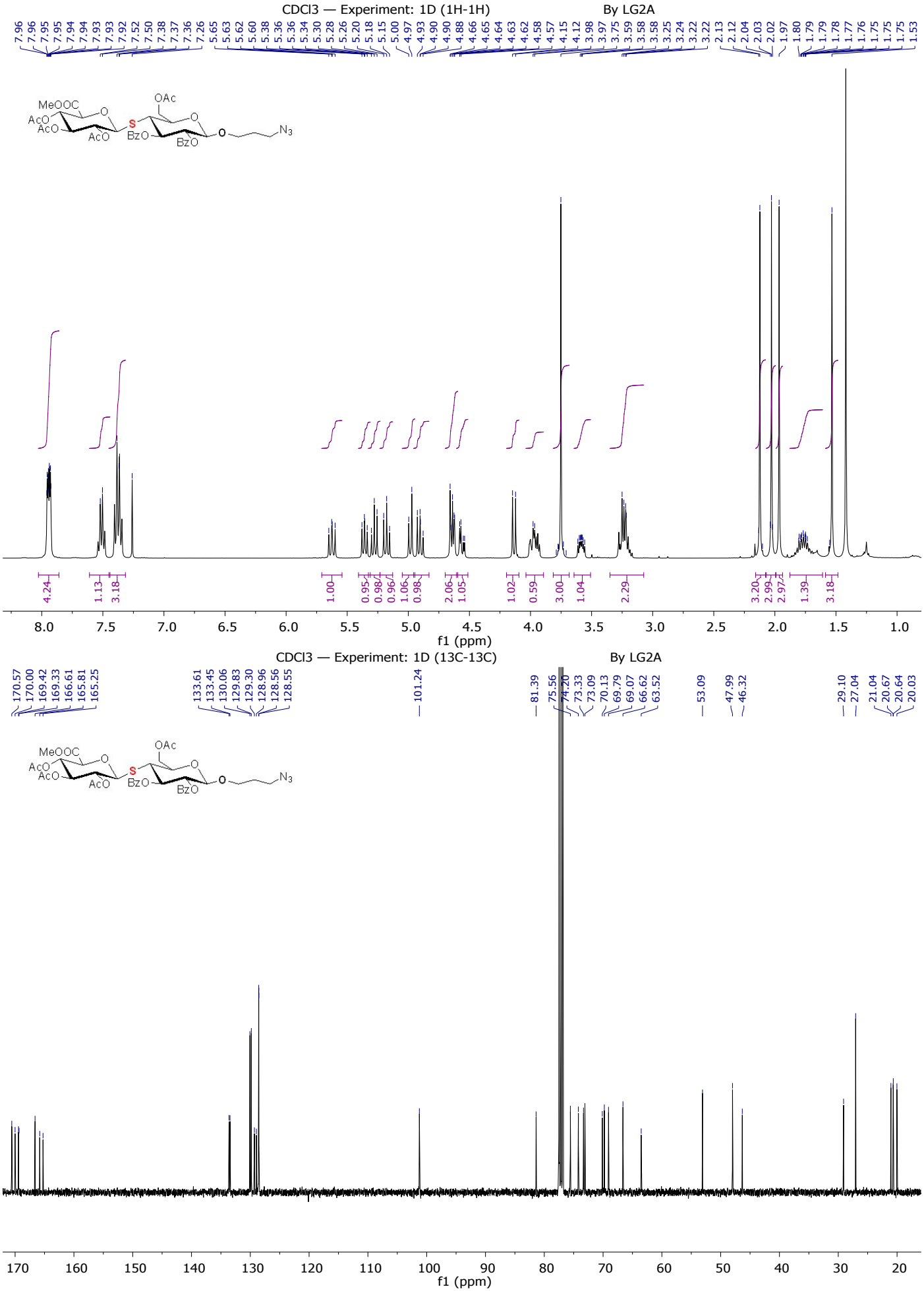


^{1}H (top) and ^{13}C (bottom) NMR spectra of **20**

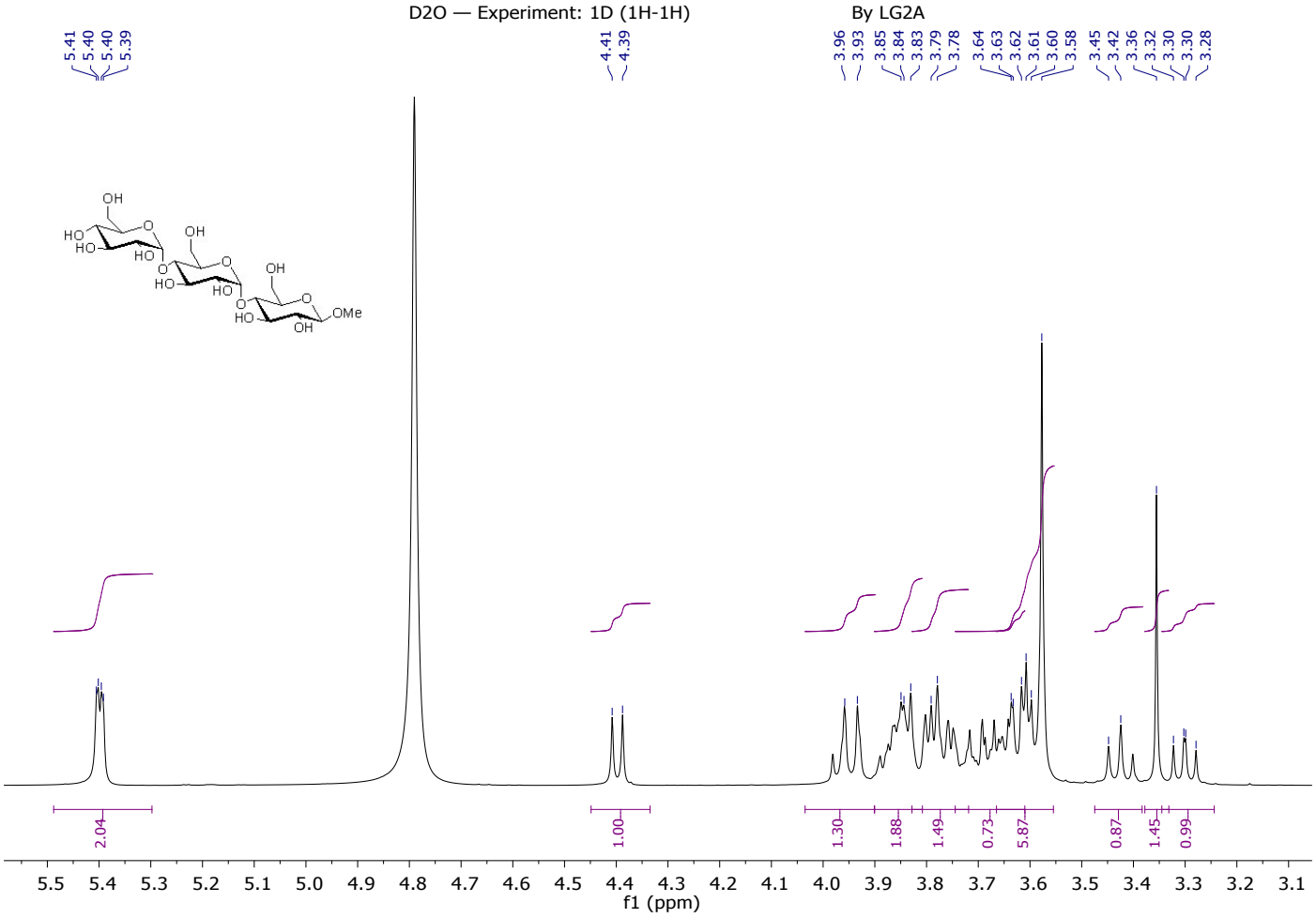


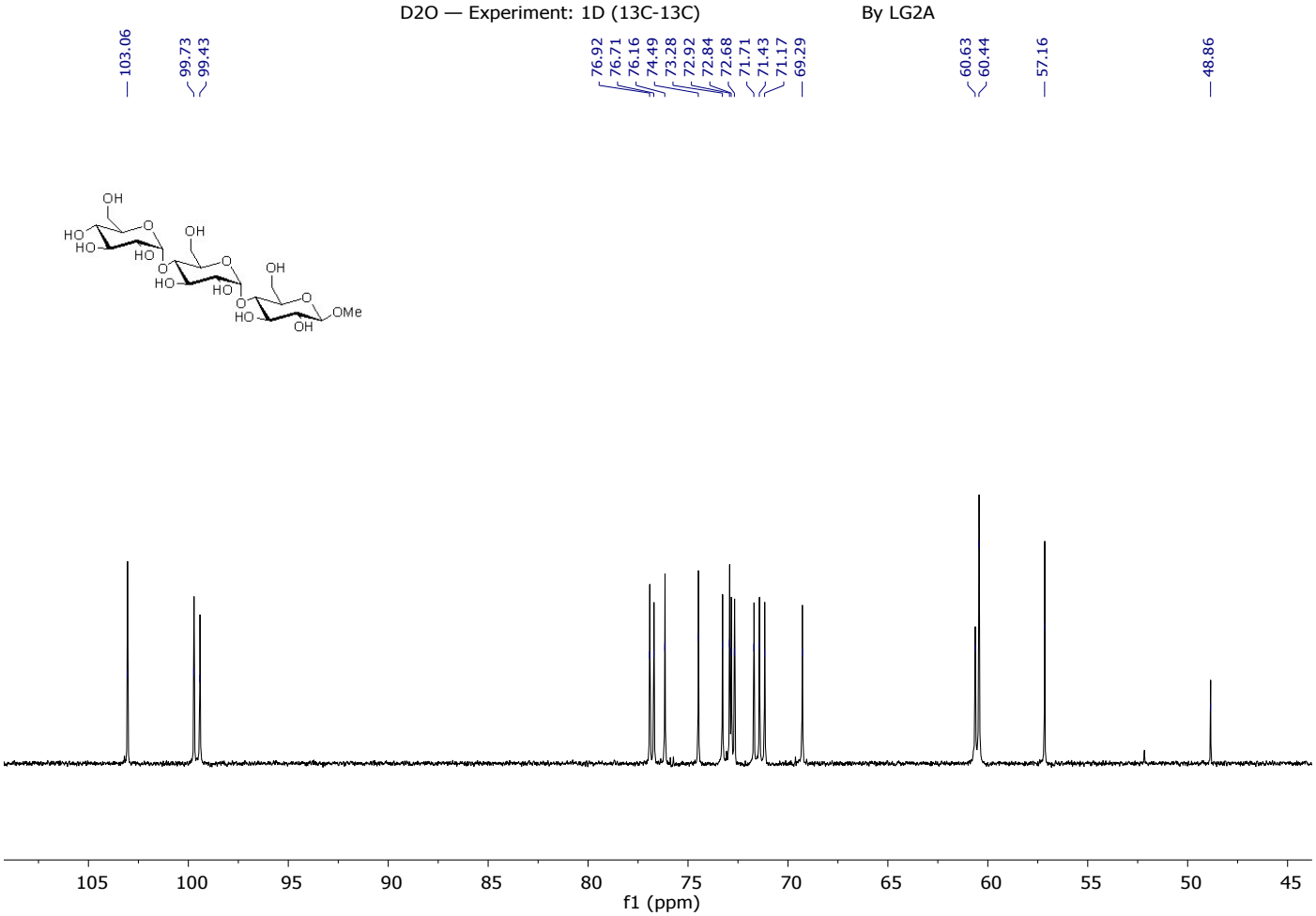


^{1}H (top) and ^{13}C (bottom) NMR spectra of **21**

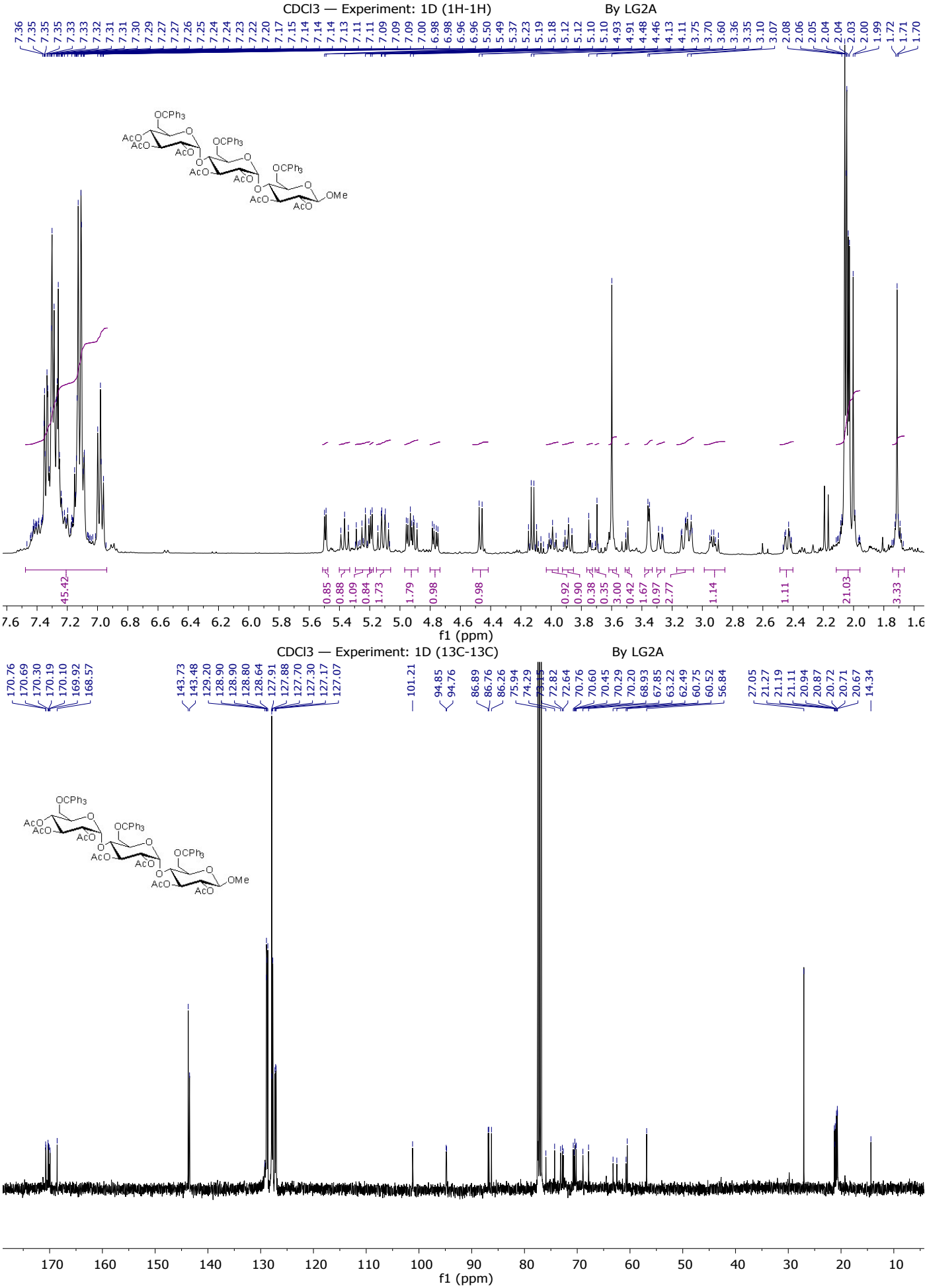


^{1}H (top) and ^{13}C (bottom) NMR spectra of **22**

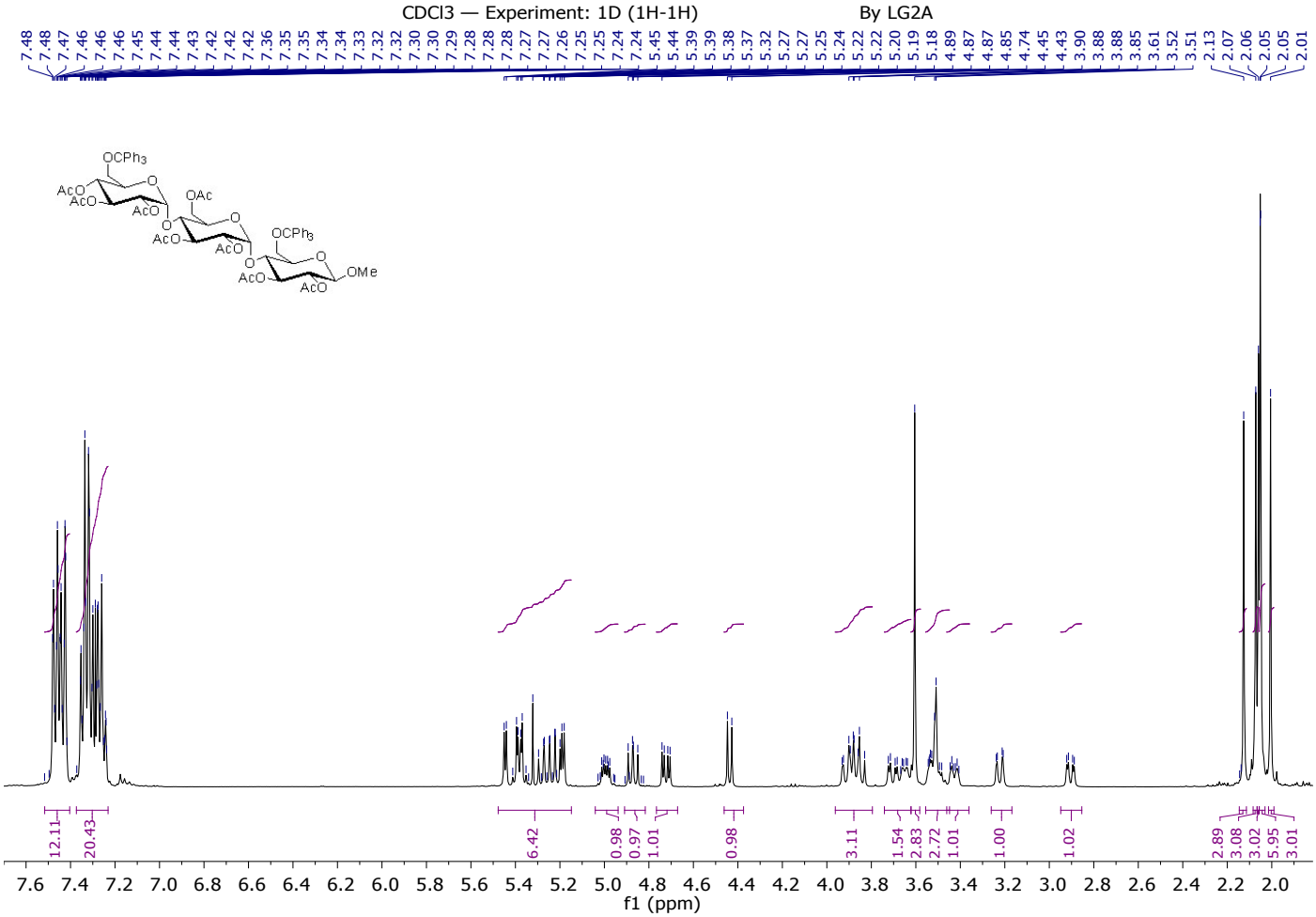


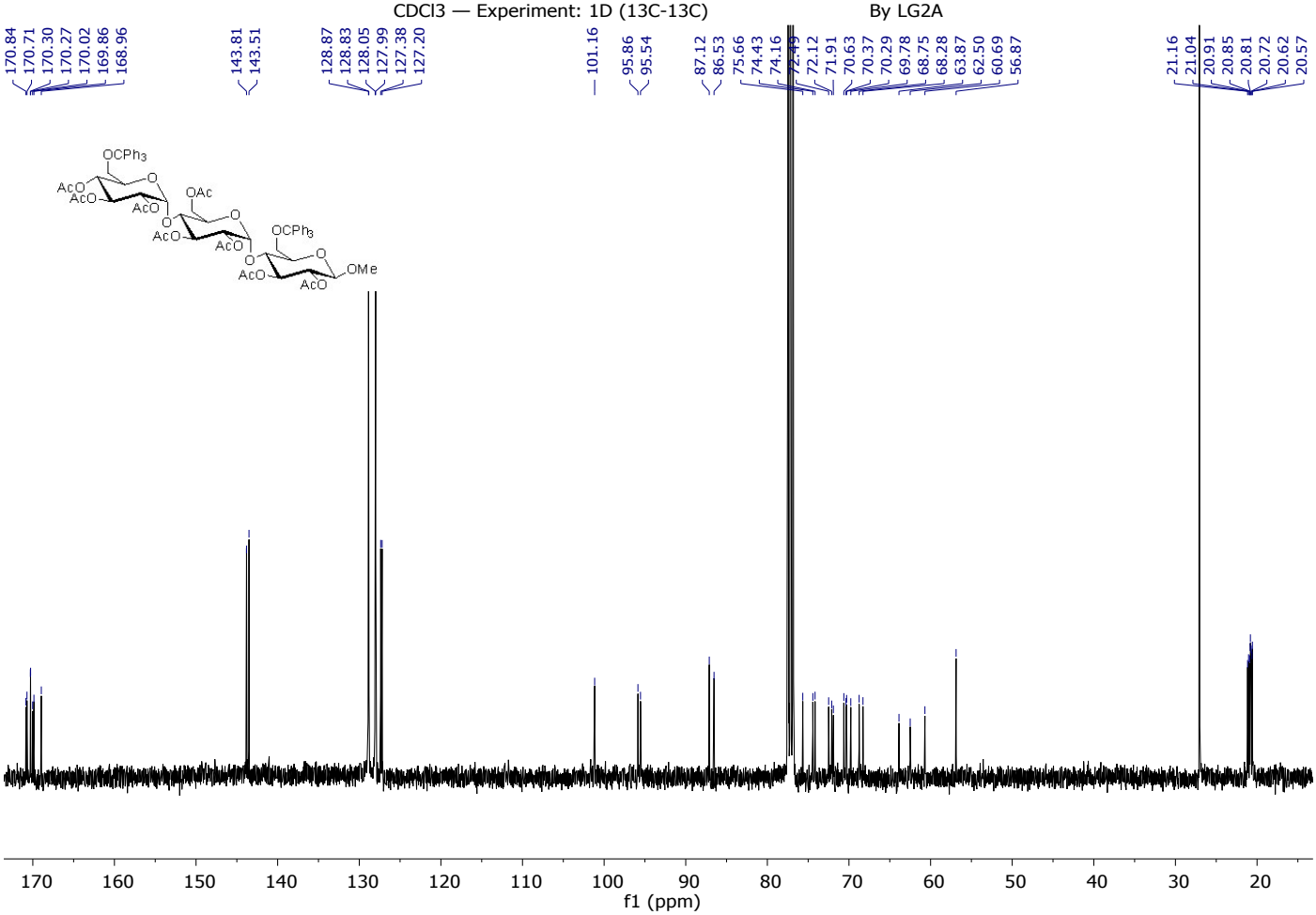


^{1}H (top) and ^{13}C (bottom) NMR spectra of **23**

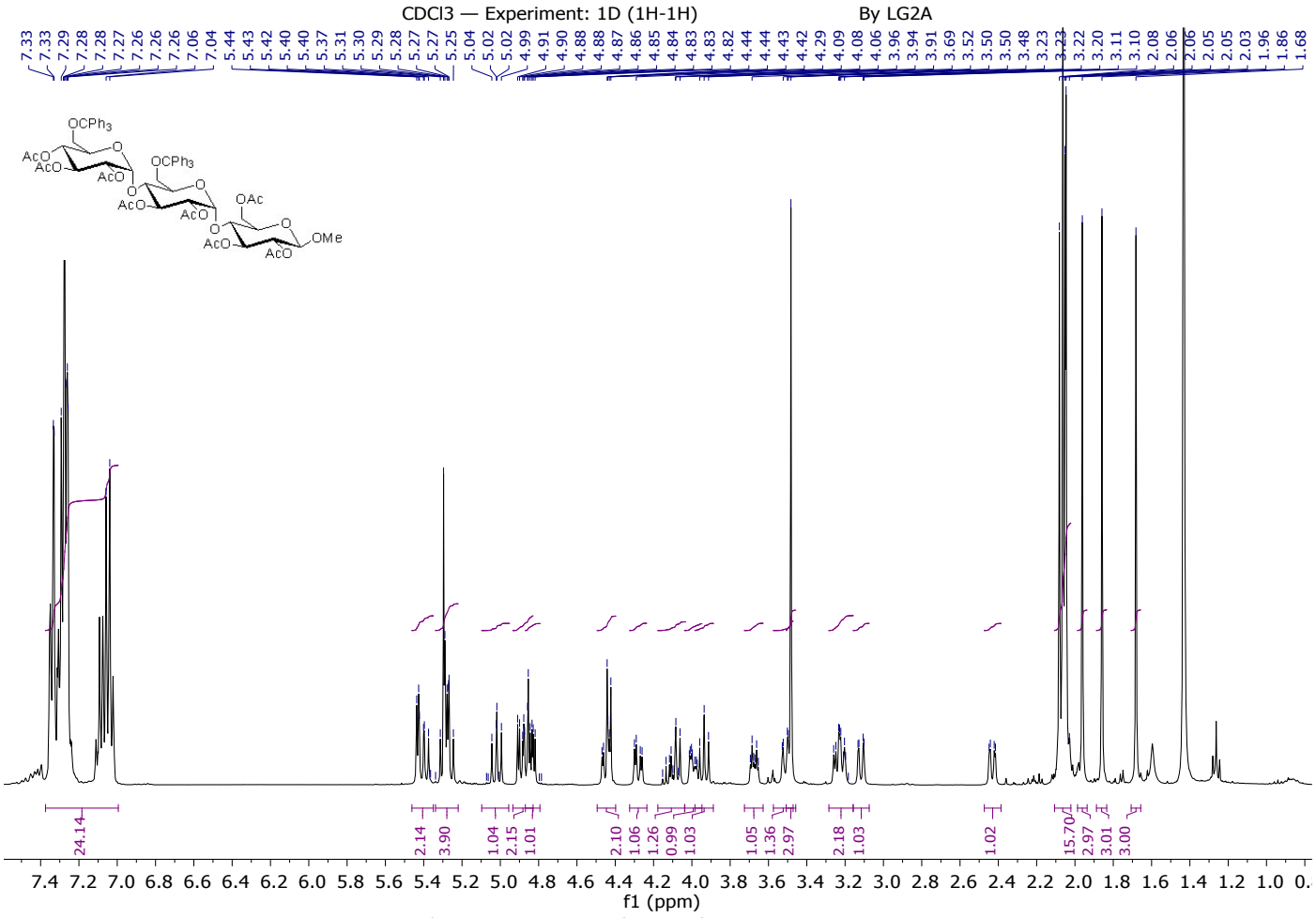


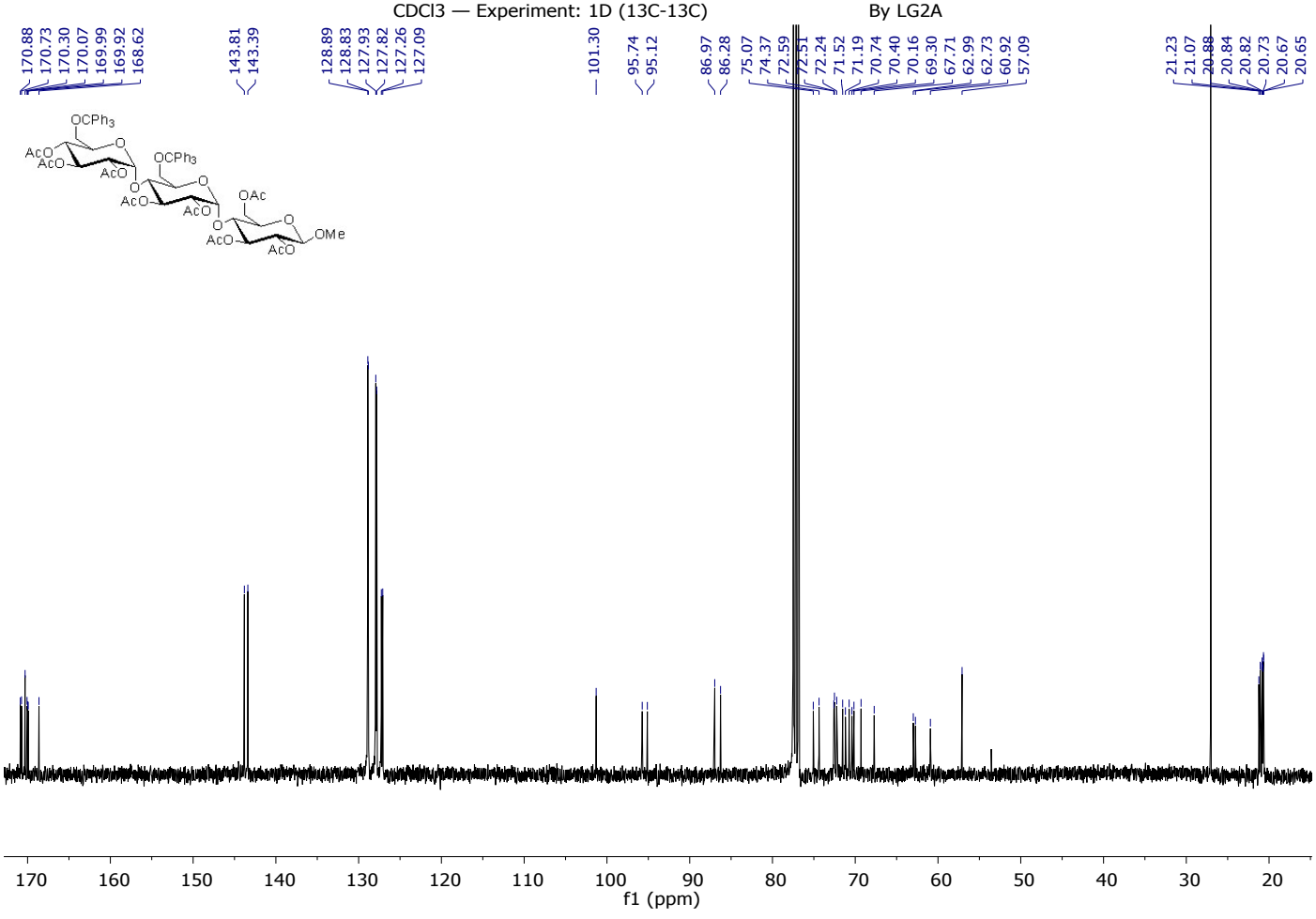
^{1}H (top) and ^{13}C (bottom) NMR spectra of **24**



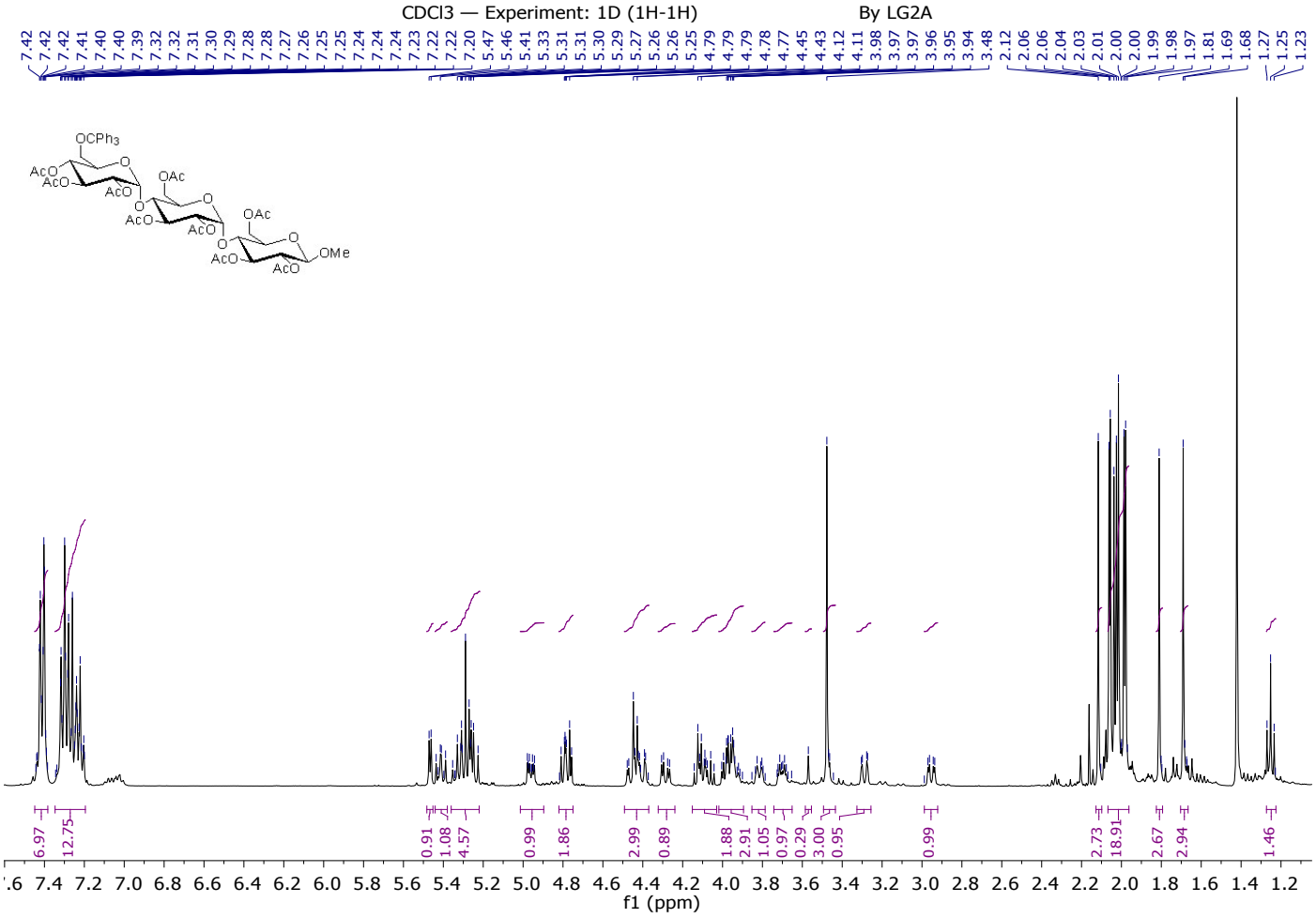


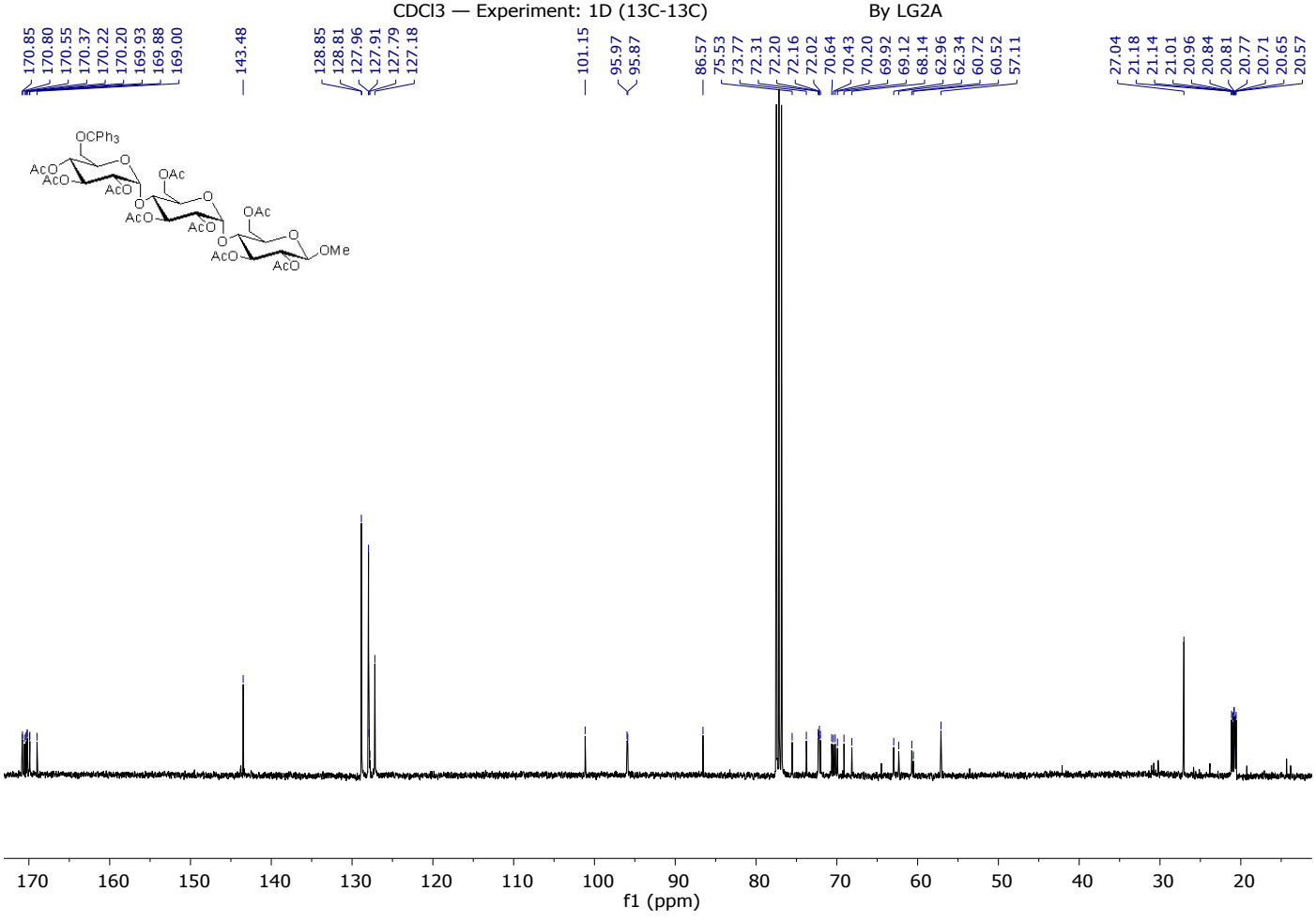
^{1}H (top) and ^{13}C (bottom) NMR spectra of **25**



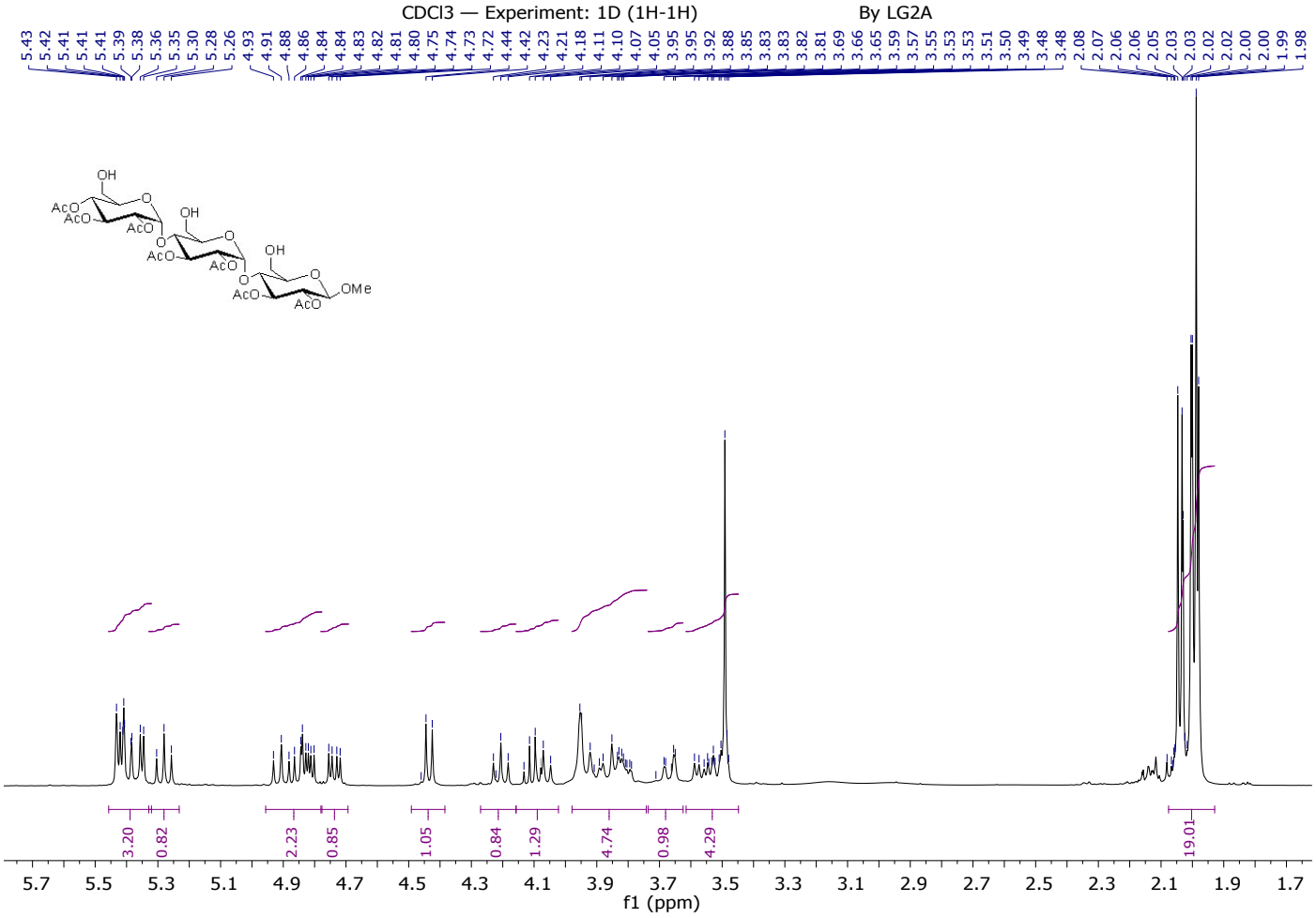


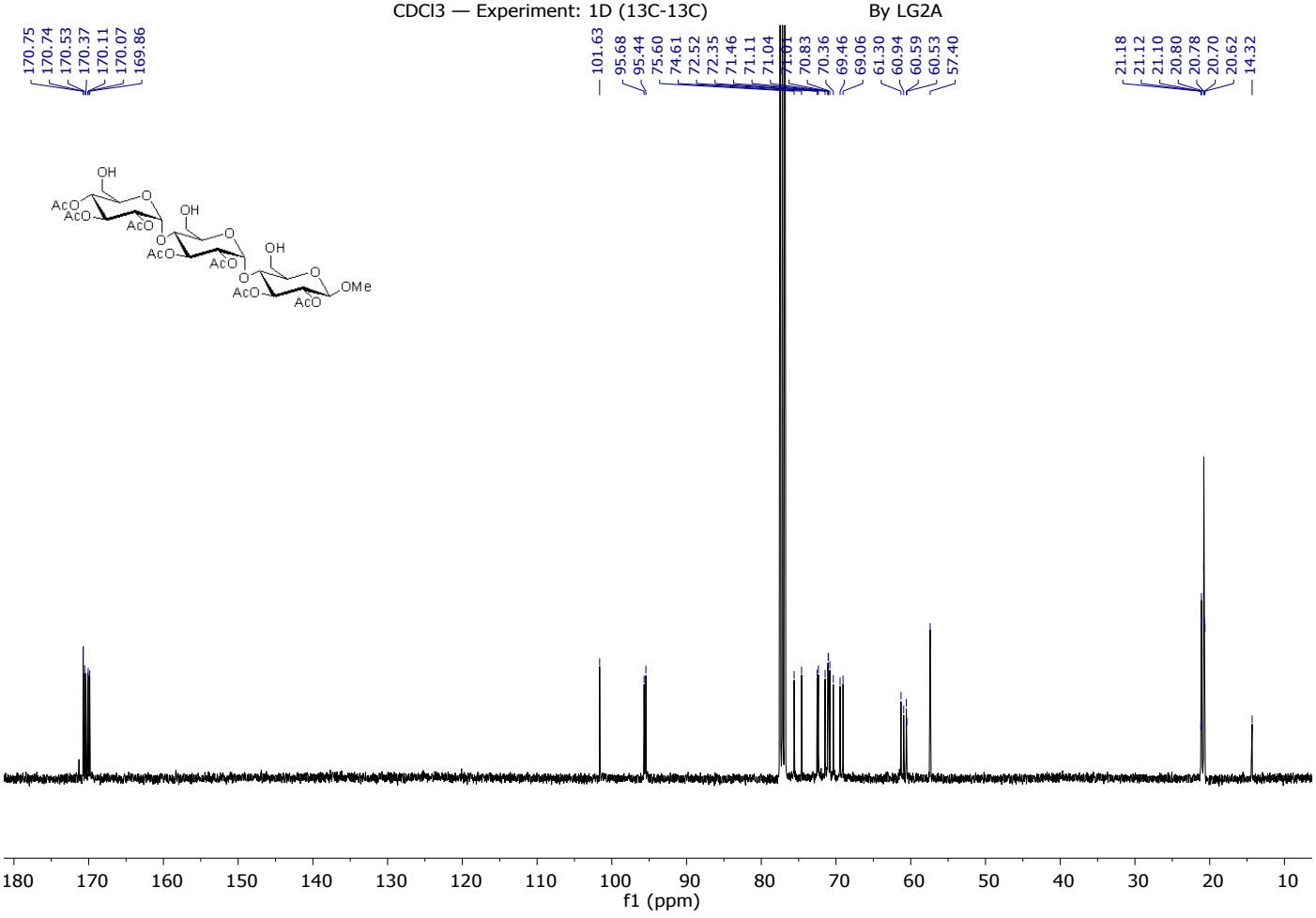
^{1}H (top) and ^{13}C (bottom) NMR spectra of **26**



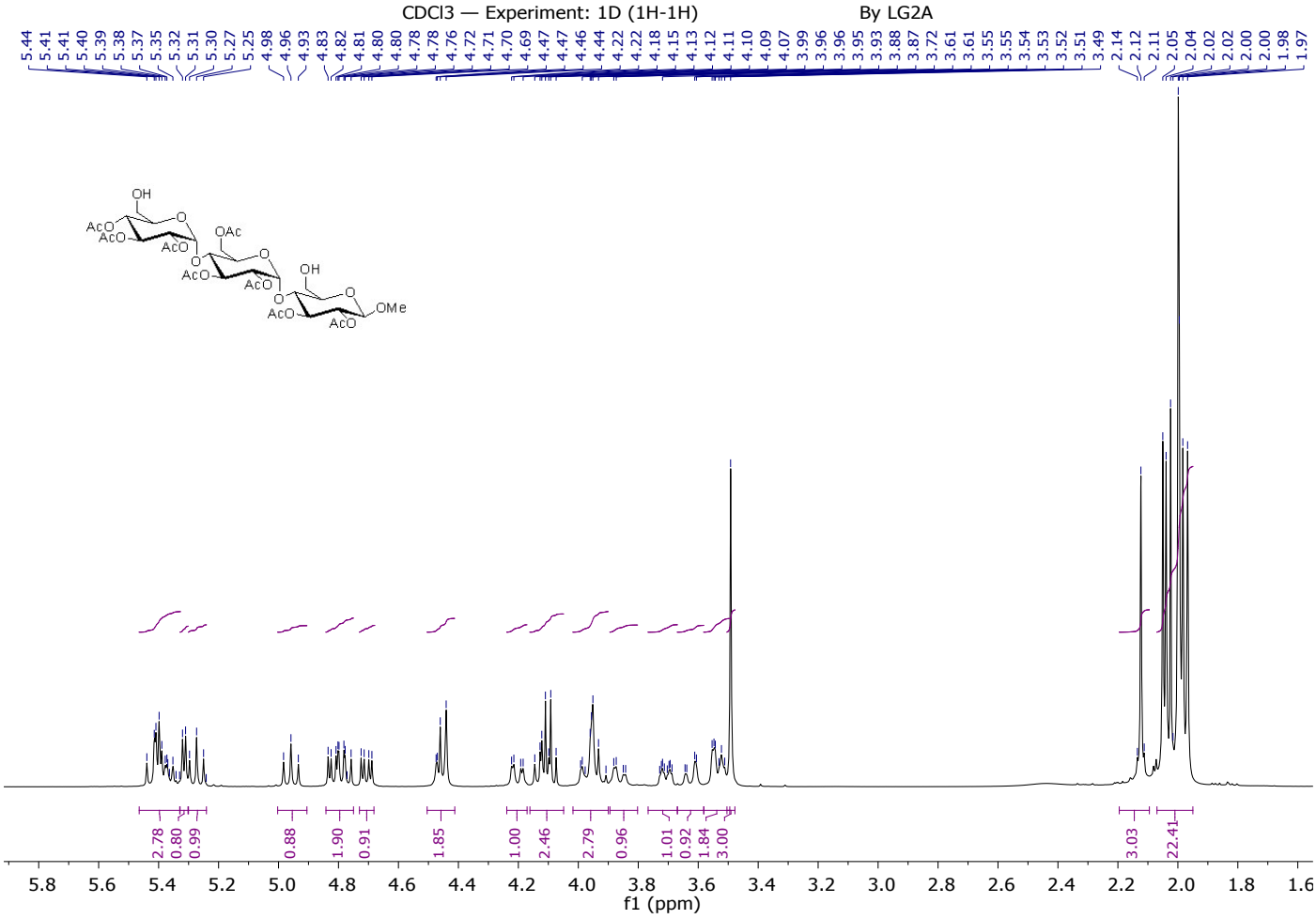


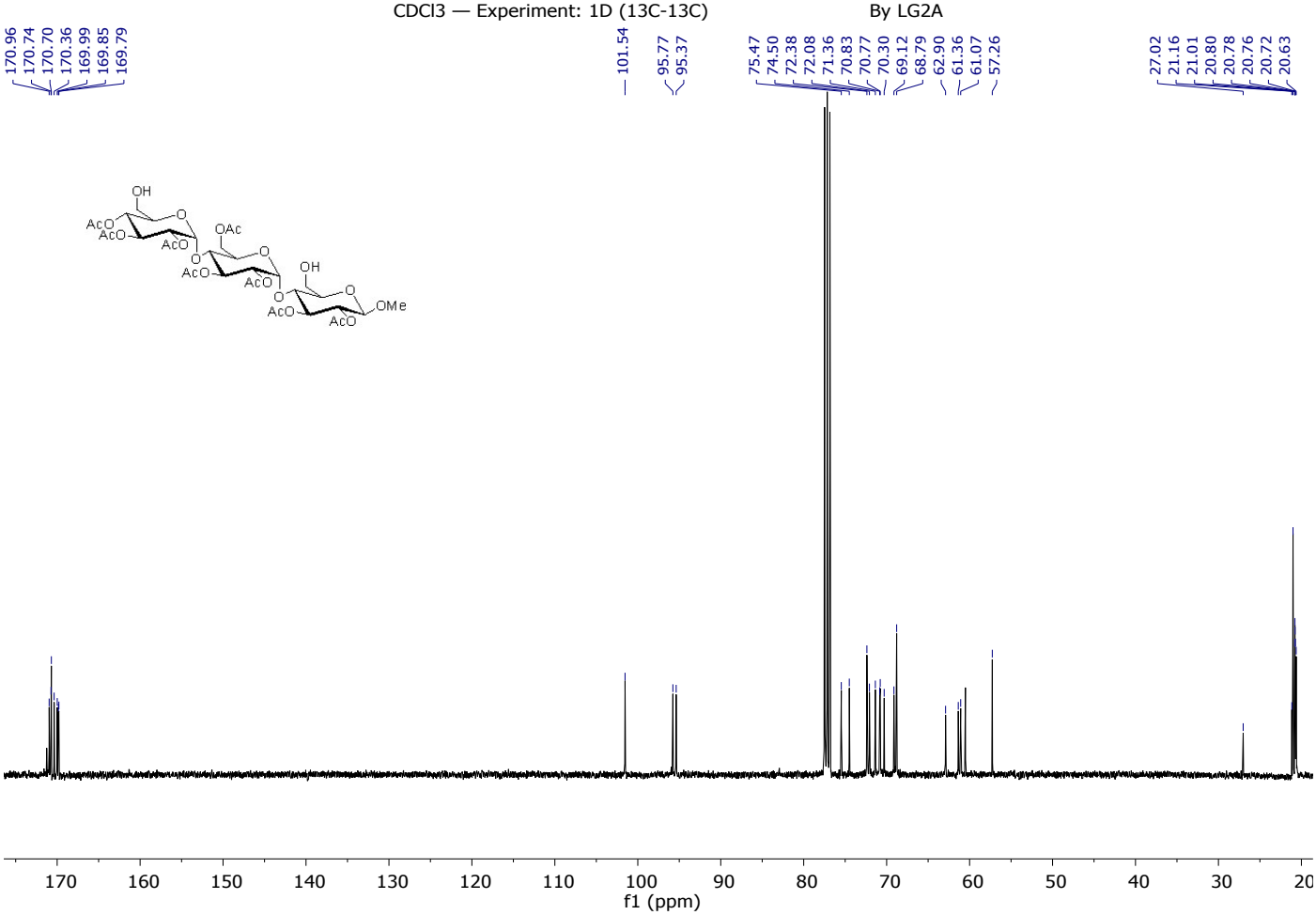
^{1}H (top) and ^{13}C (bottom) NMR spectra of **27**



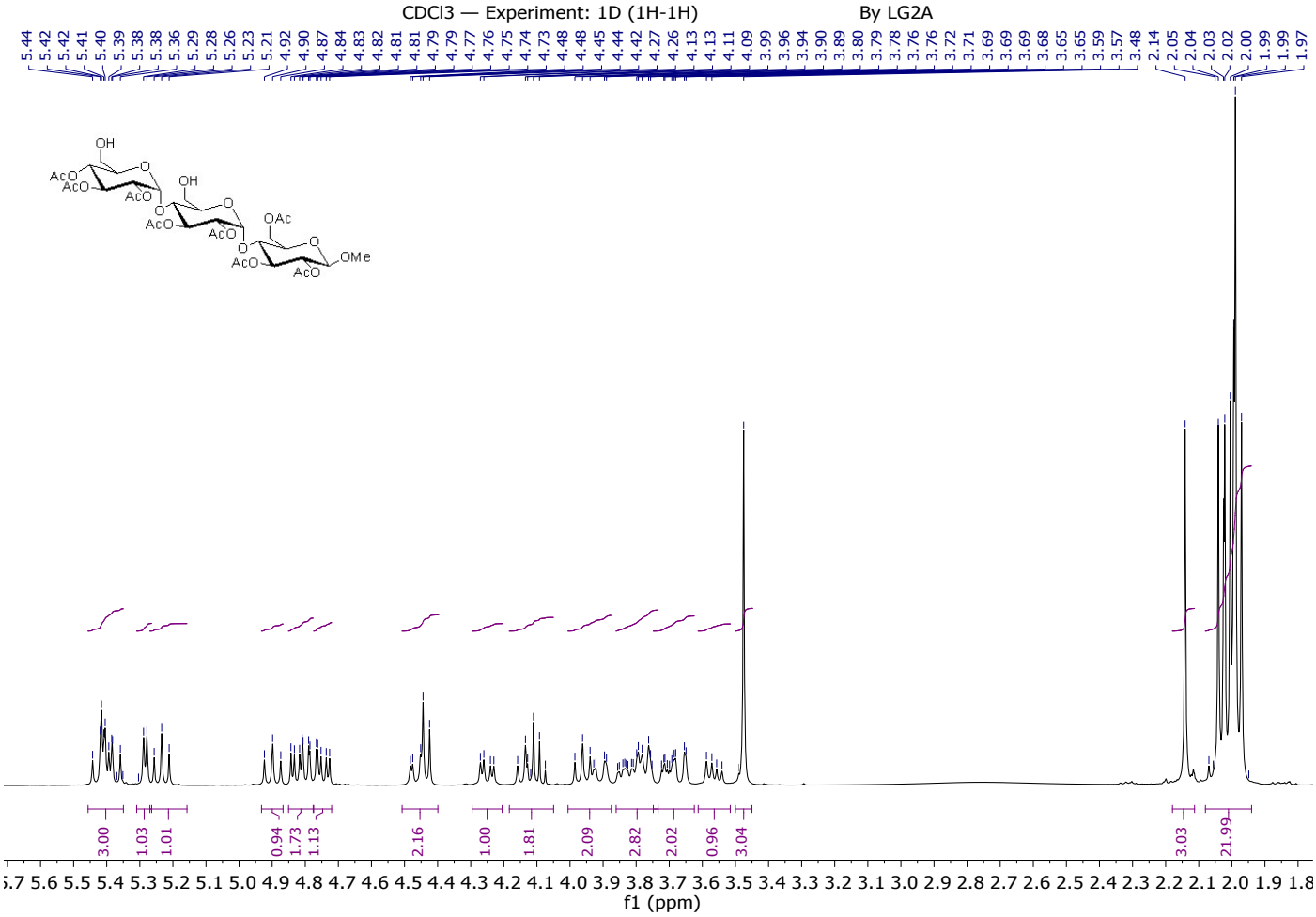


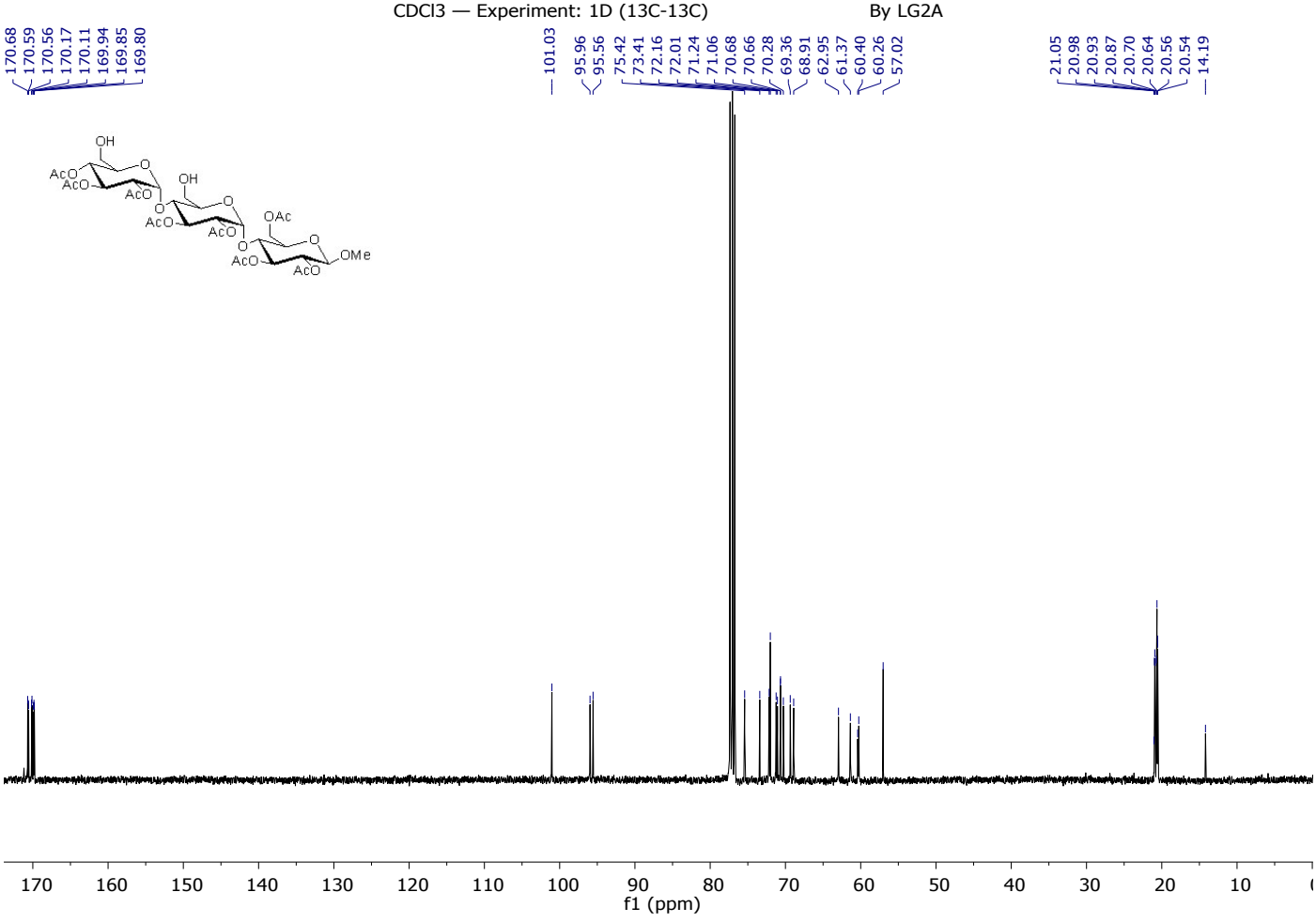
^{1}H (top) and ^{13}C (bottom) NMR spectra of **28**



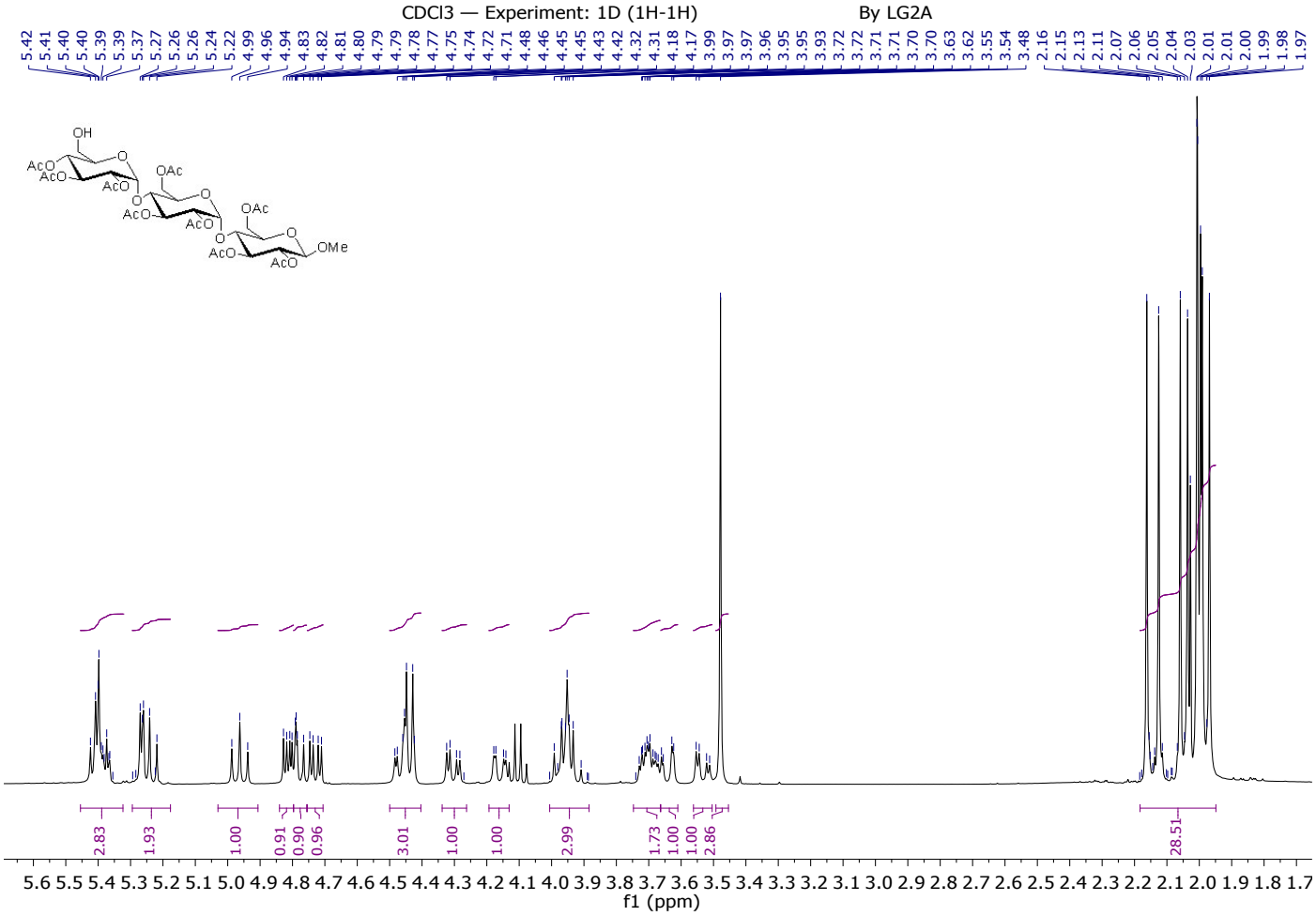


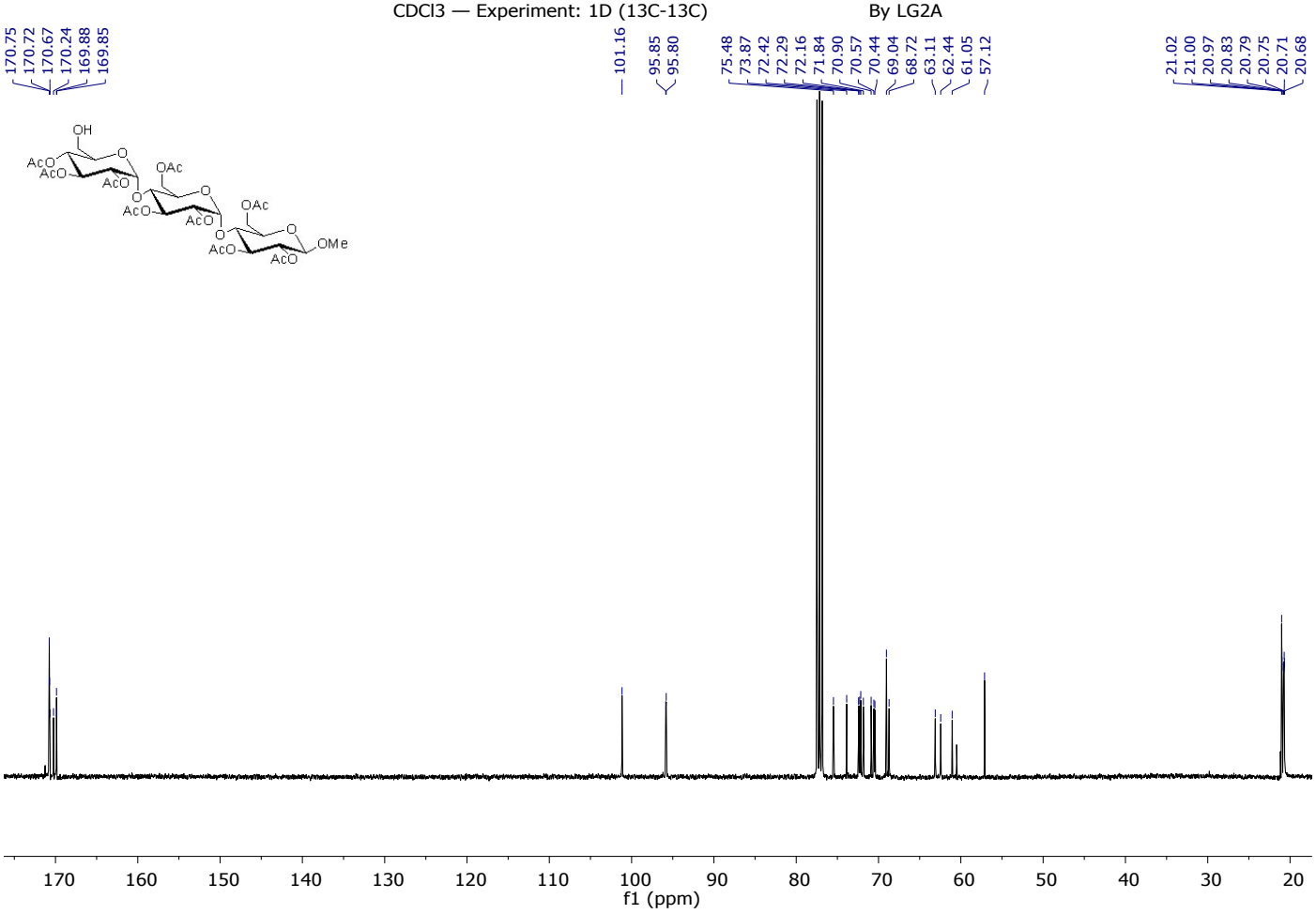
^{1}H (top) and ^{13}C (bottom) NMR spectra of **29**



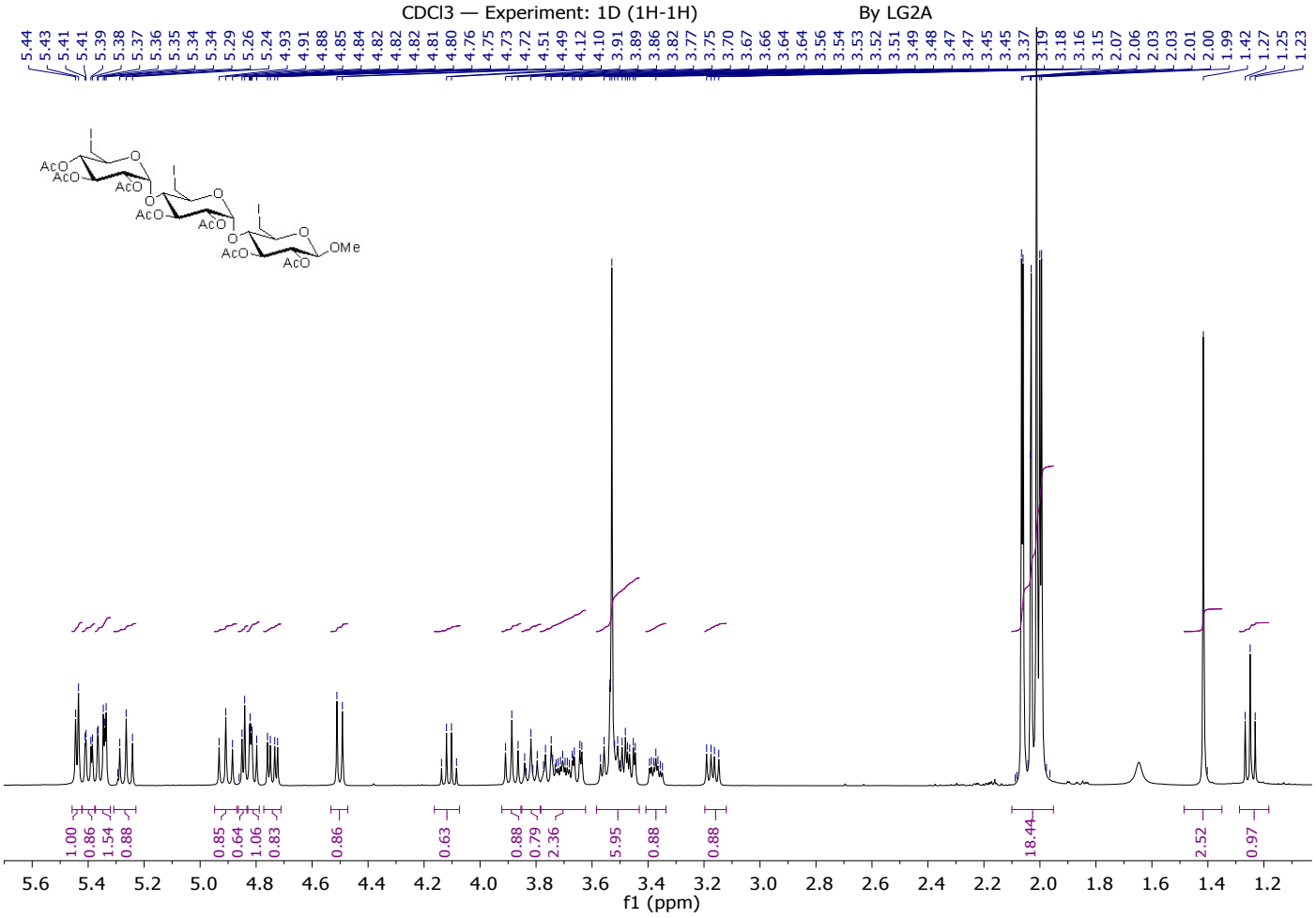


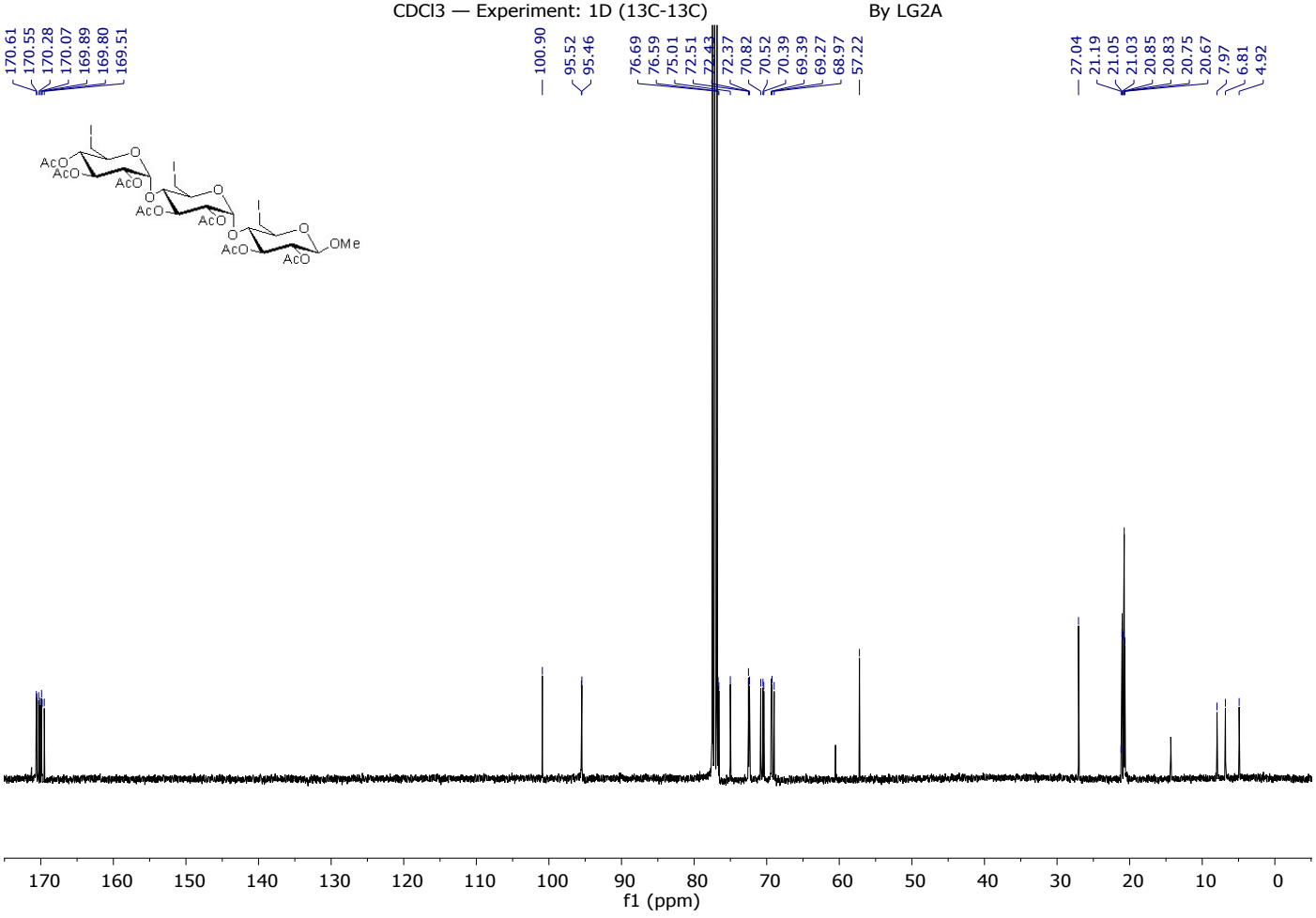
^{1}H (top) and ^{13}C (bottom) NMR spectra of **30**



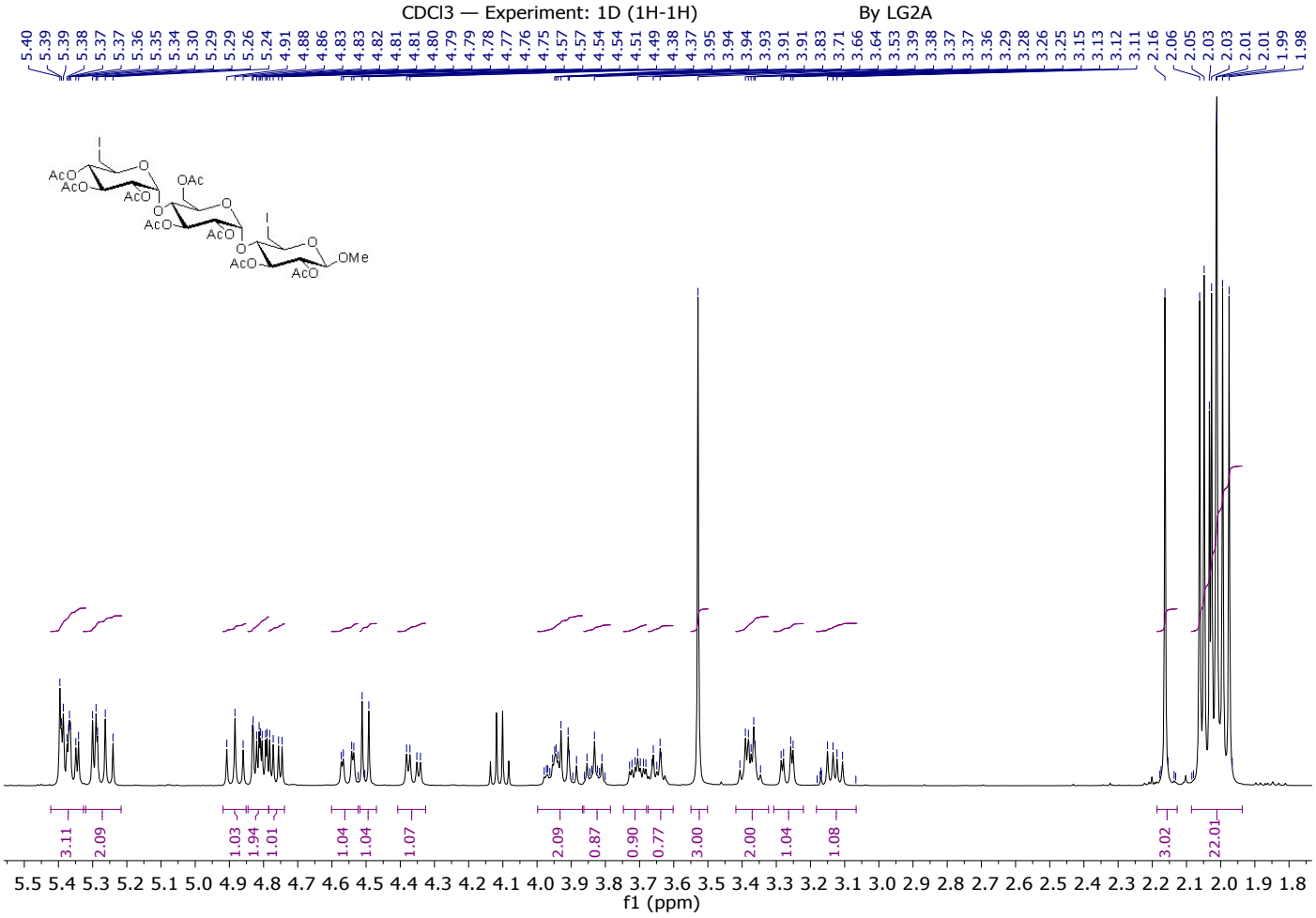


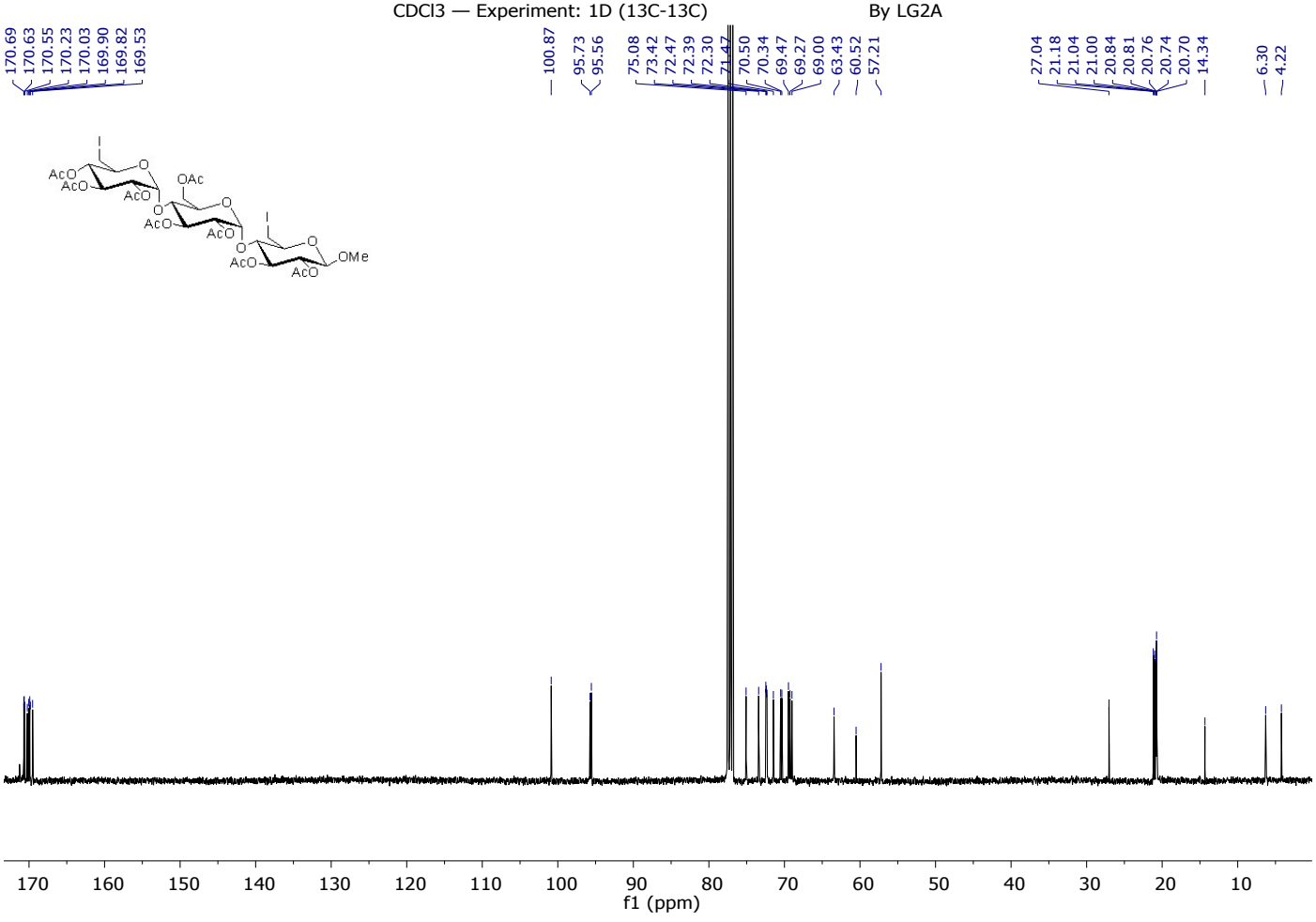
^{1}H (top) and ^{13}C (bottom) NMR spectra of **31**



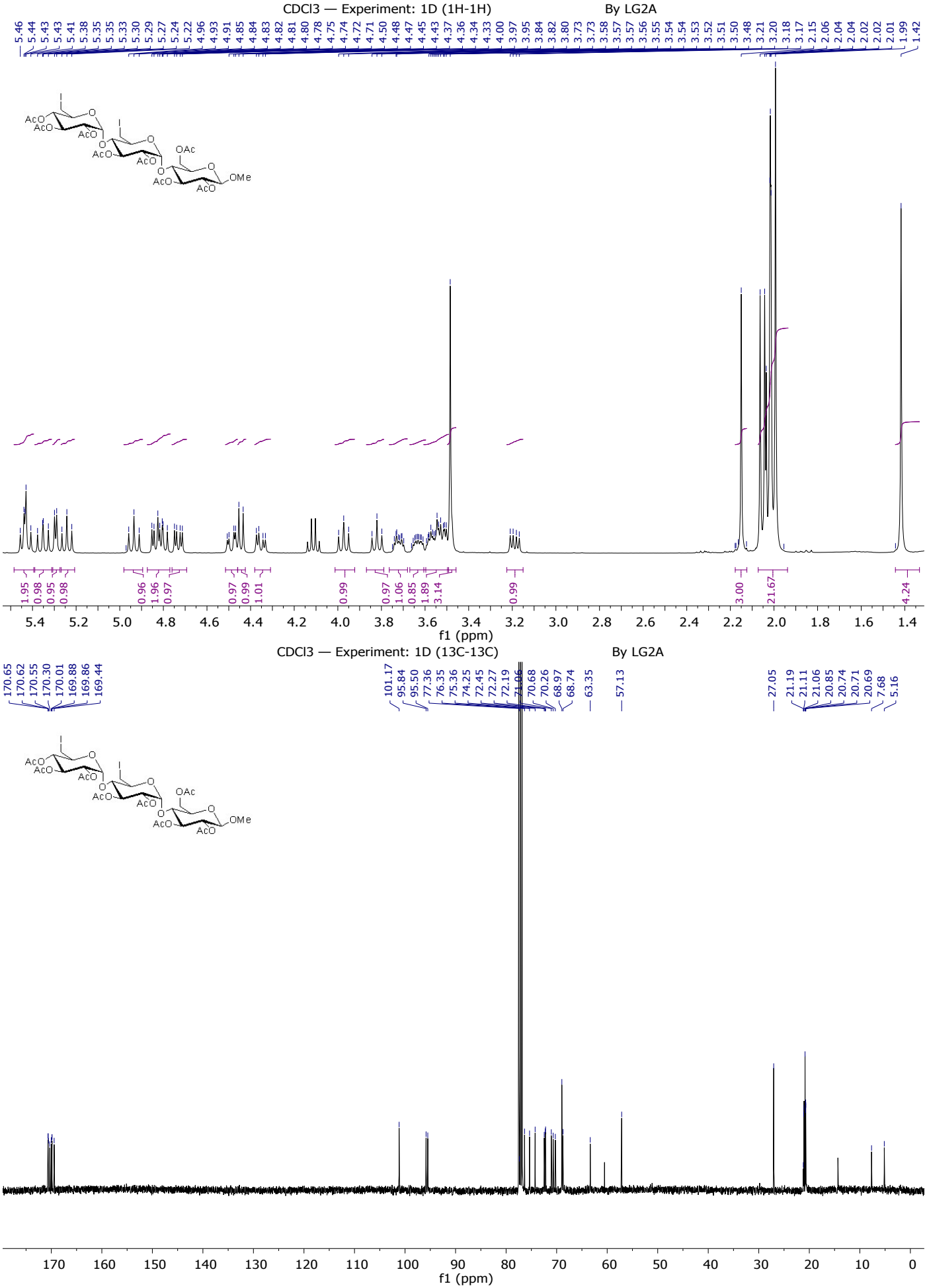


^{1}H (top) and ^{13}C (bottom) NMR spectra of **32**

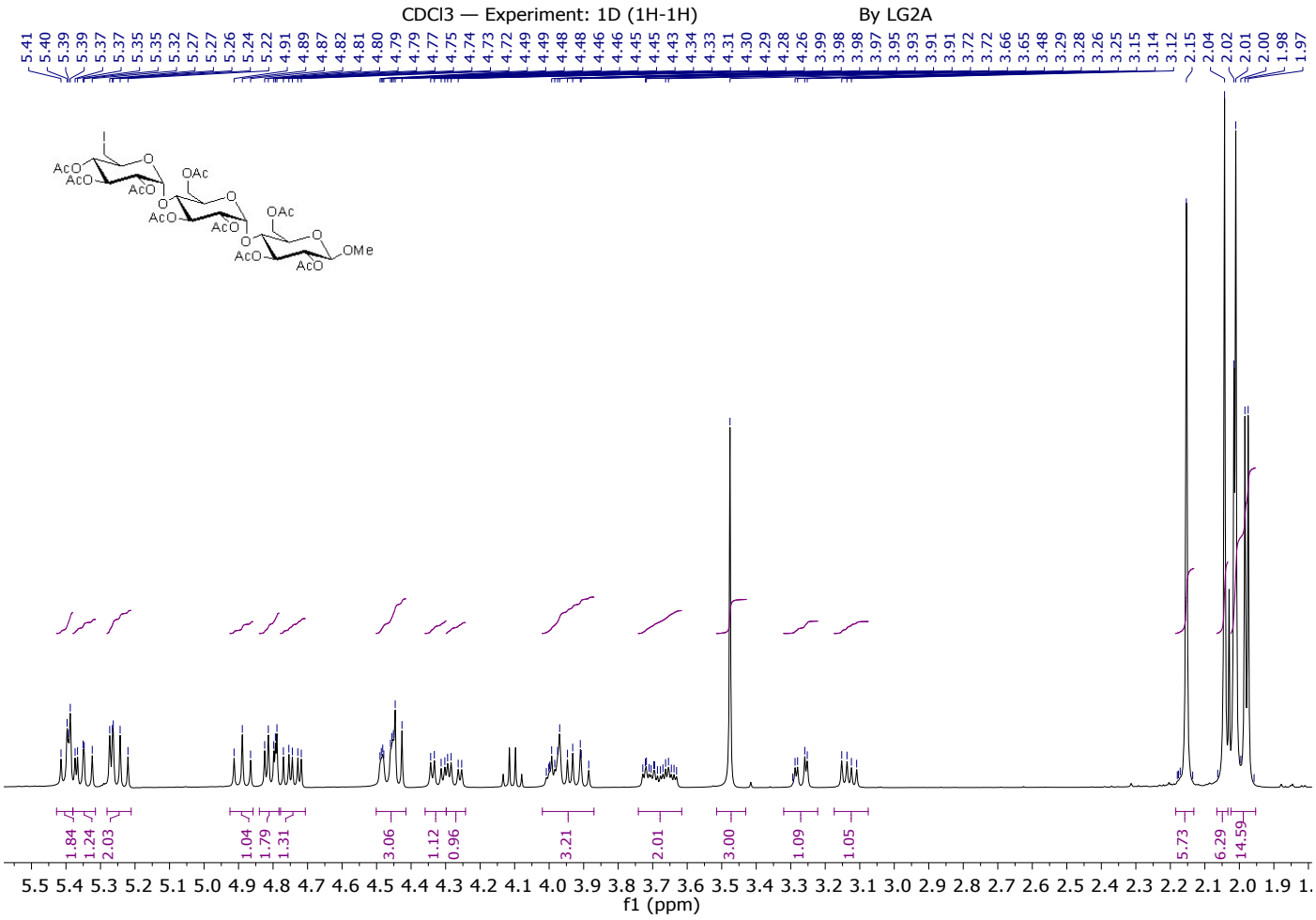


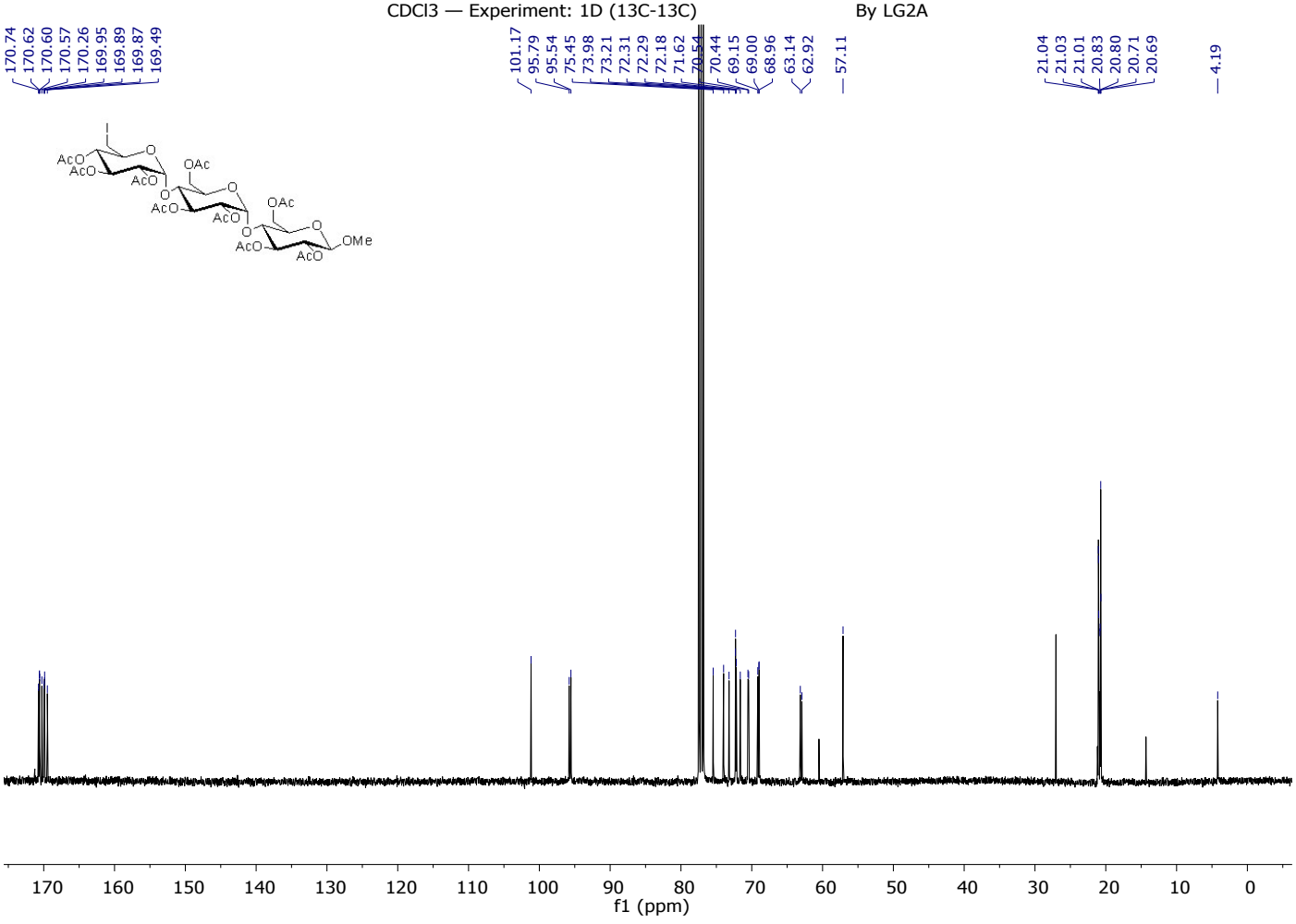


^{1}H (top) and ^{13}C (bottom) NMR spectra of **33**

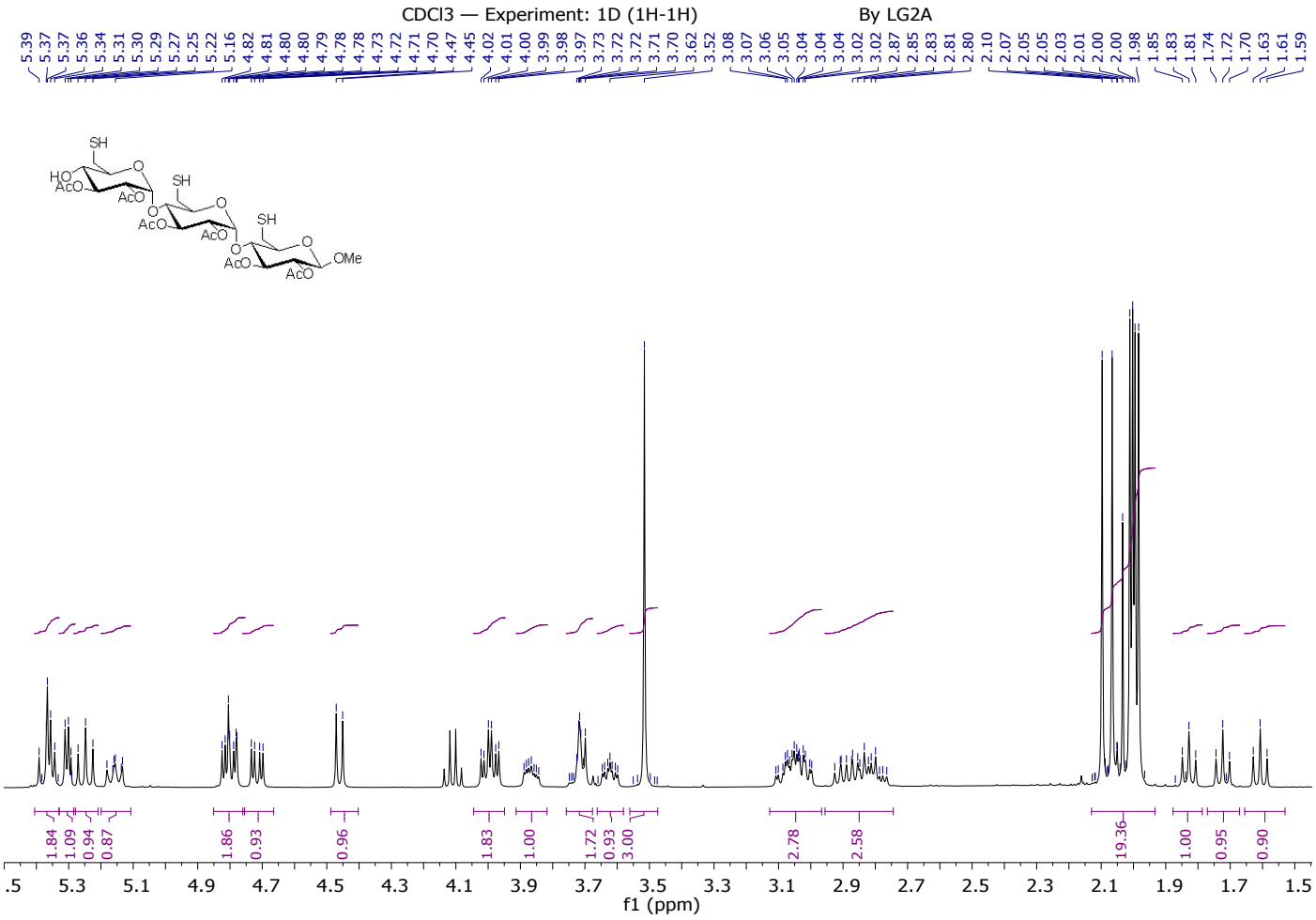


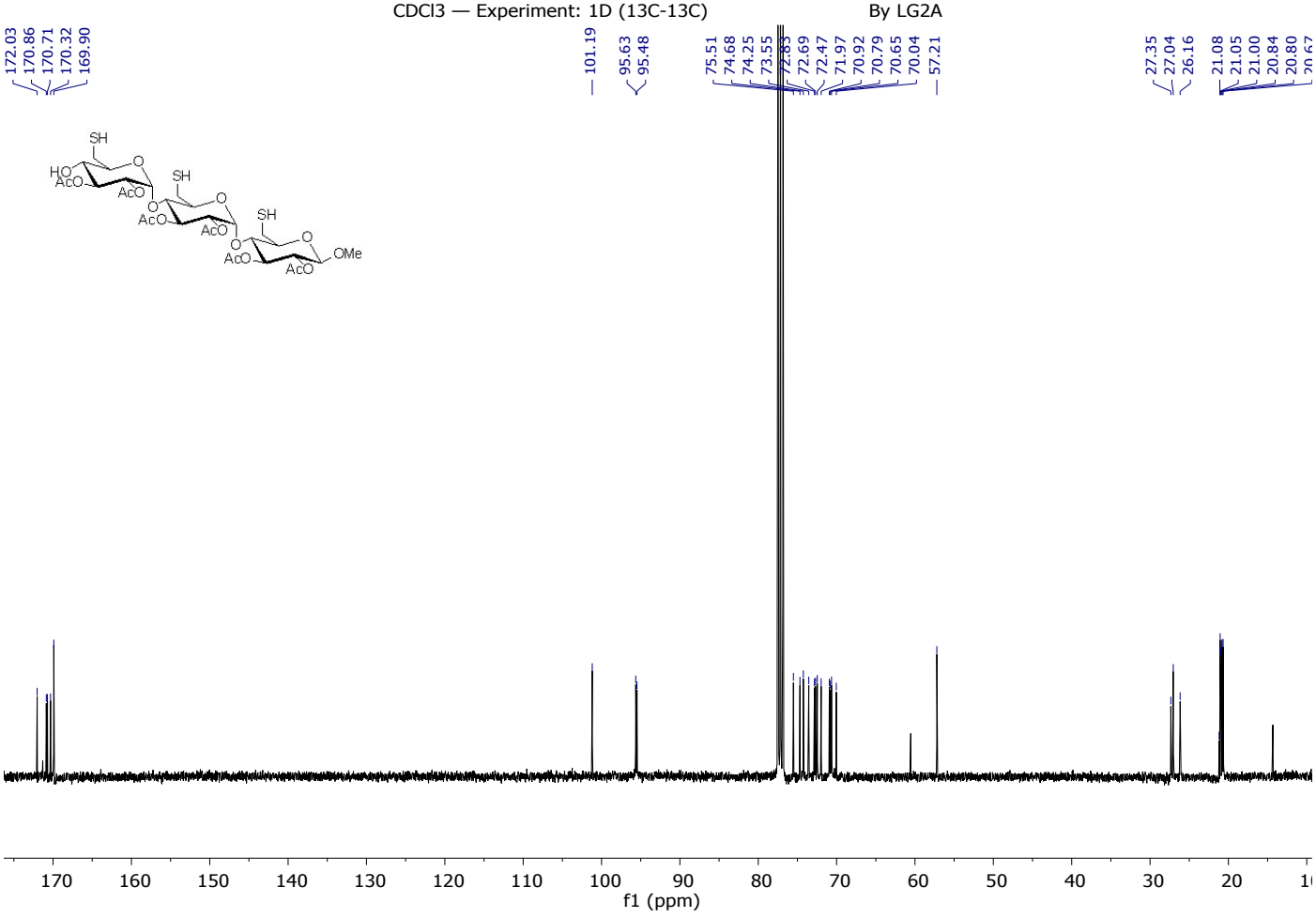
^{1}H (top) and ^{13}C (bottom) NMR spectra of **34**



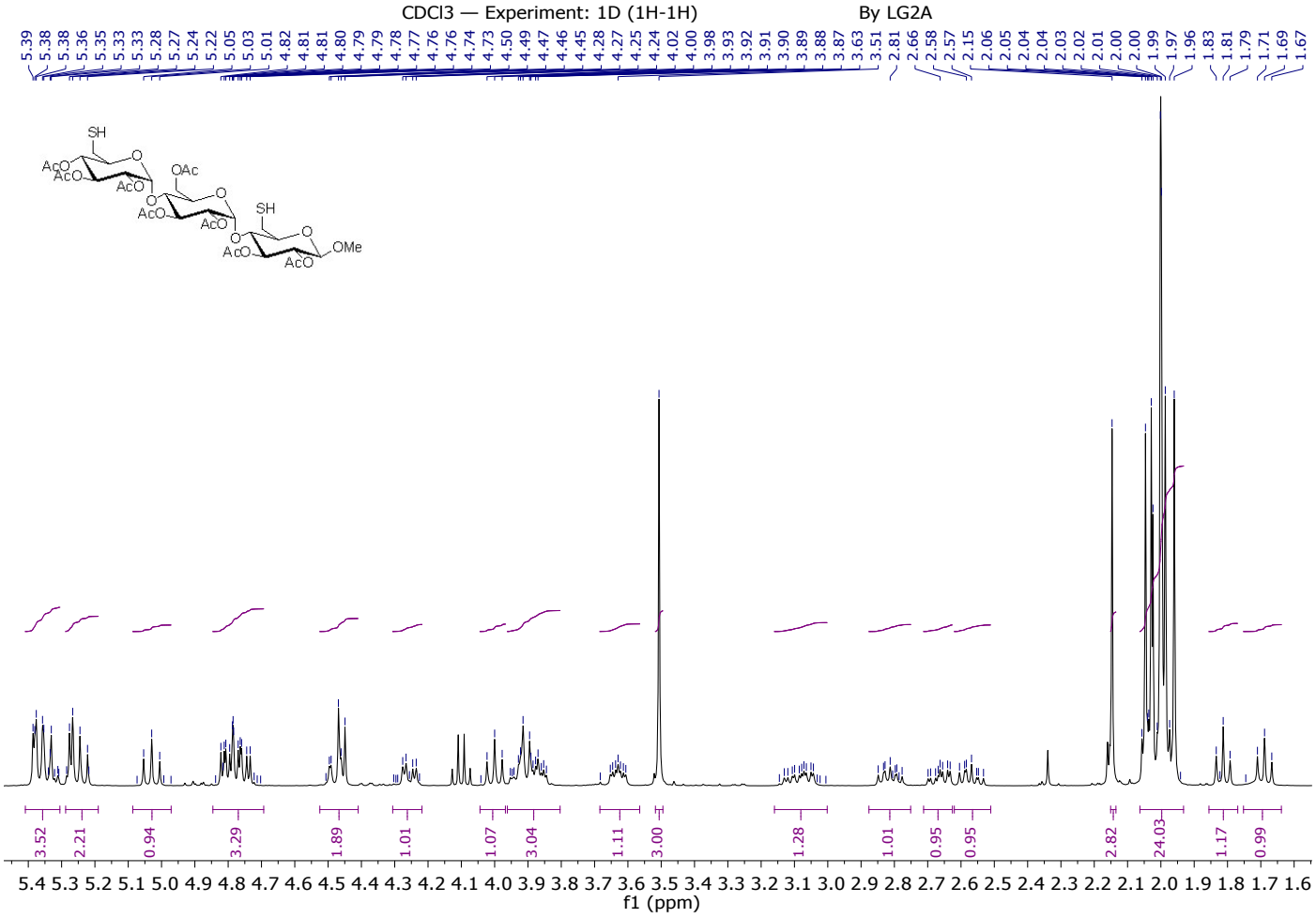


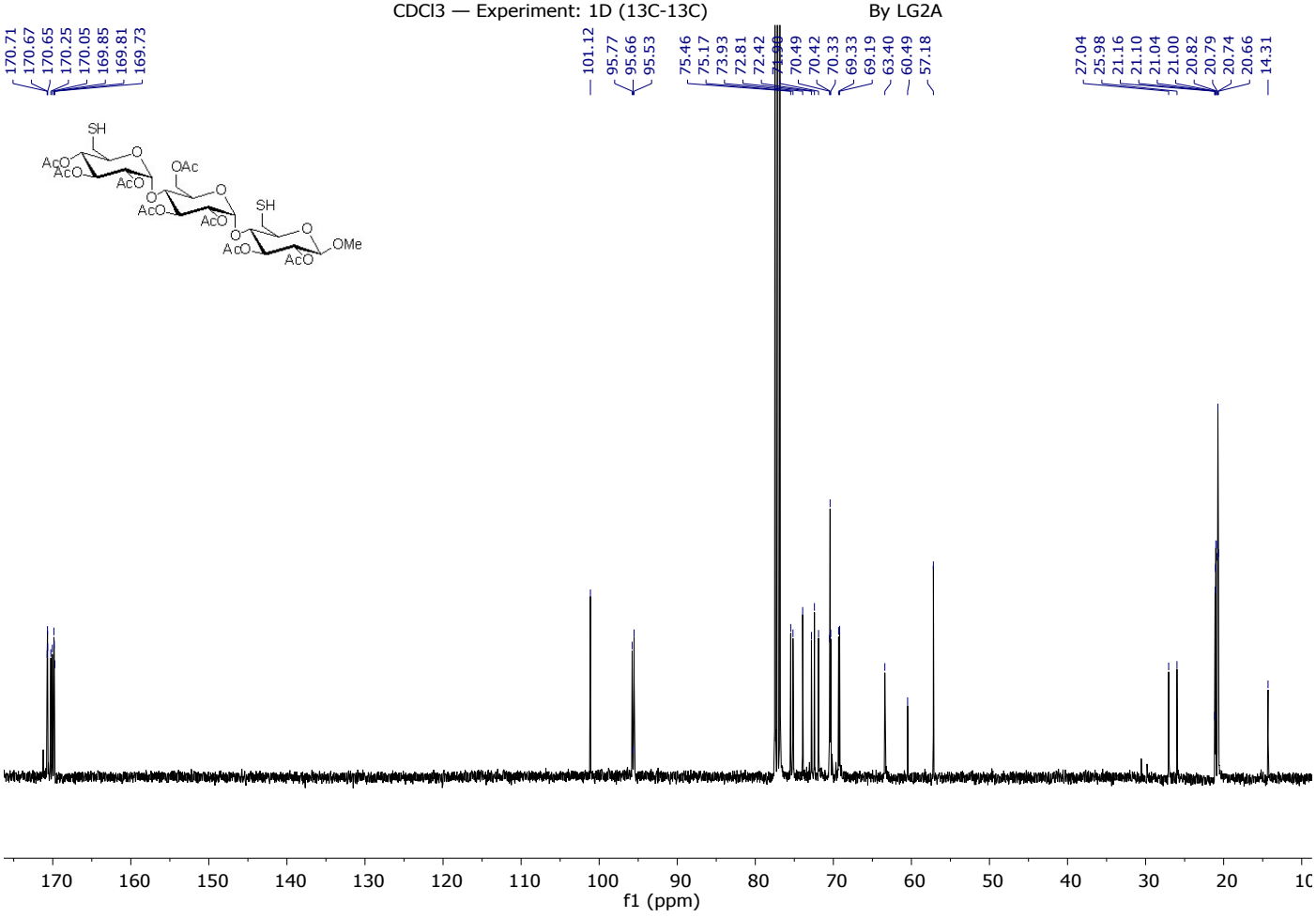
^{1}H (top) and ^{13}C (bottom) NMR spectra of **35**



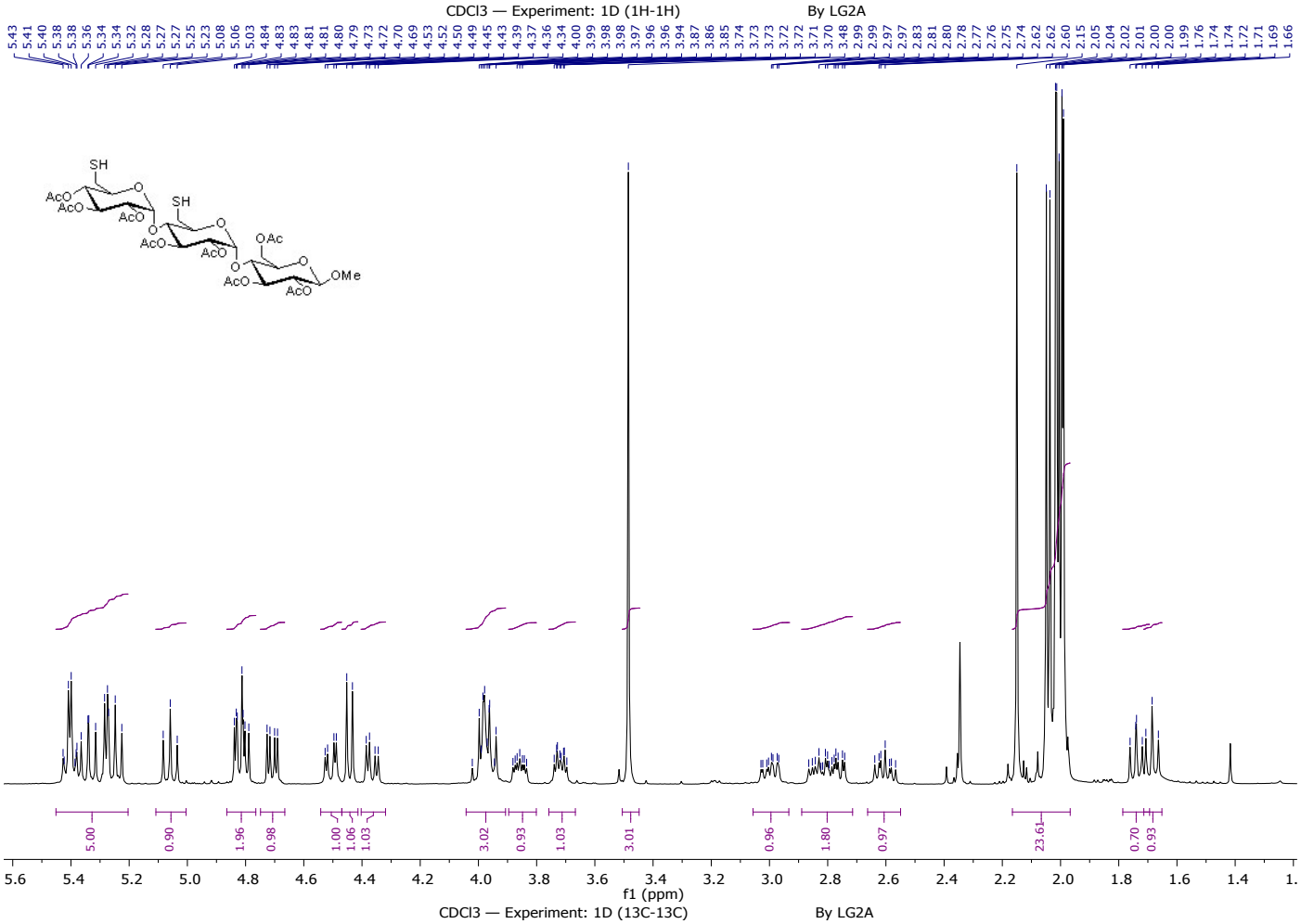


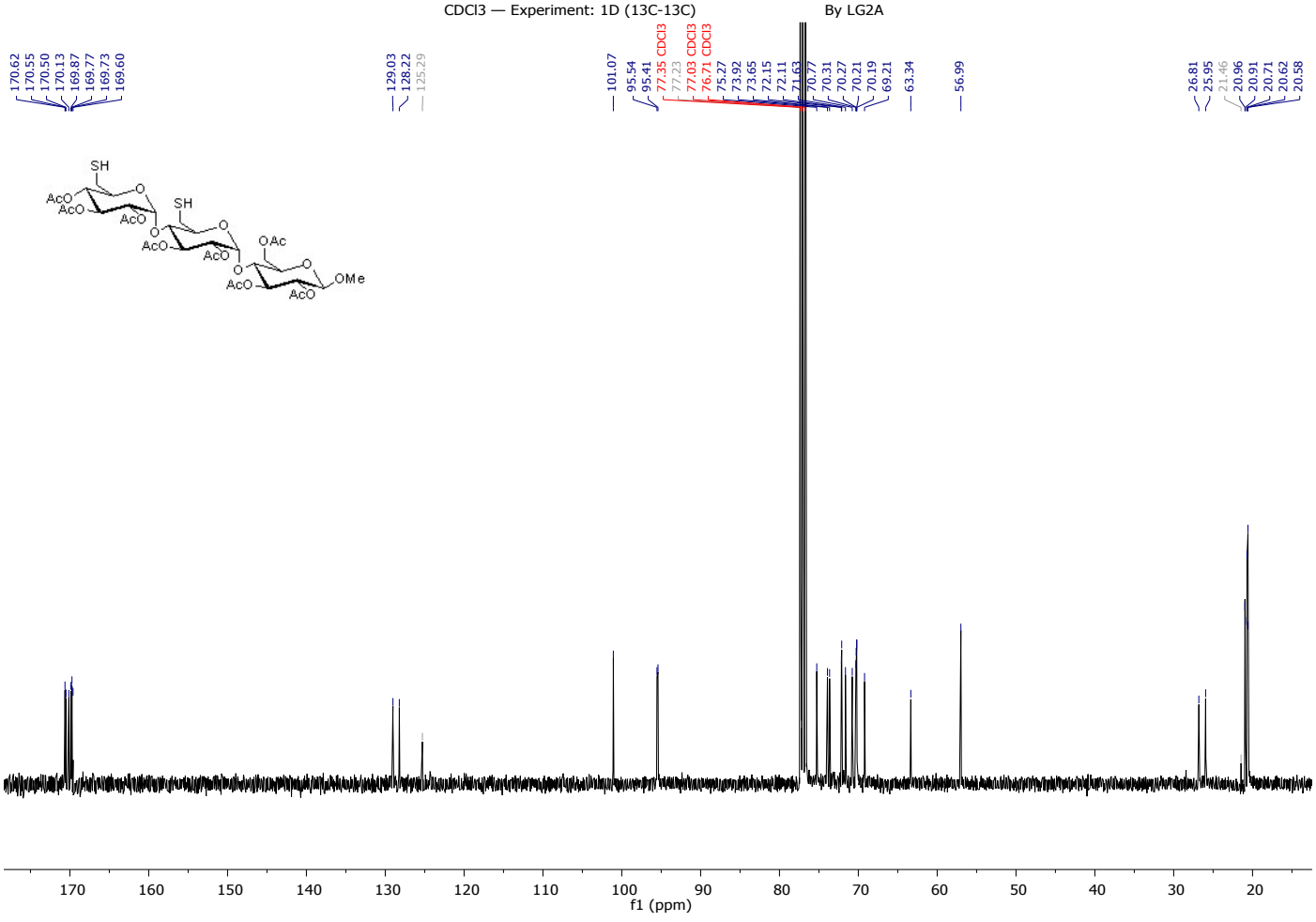
^{1}H (top) and ^{13}C (bottom) NMR spectra of **36**



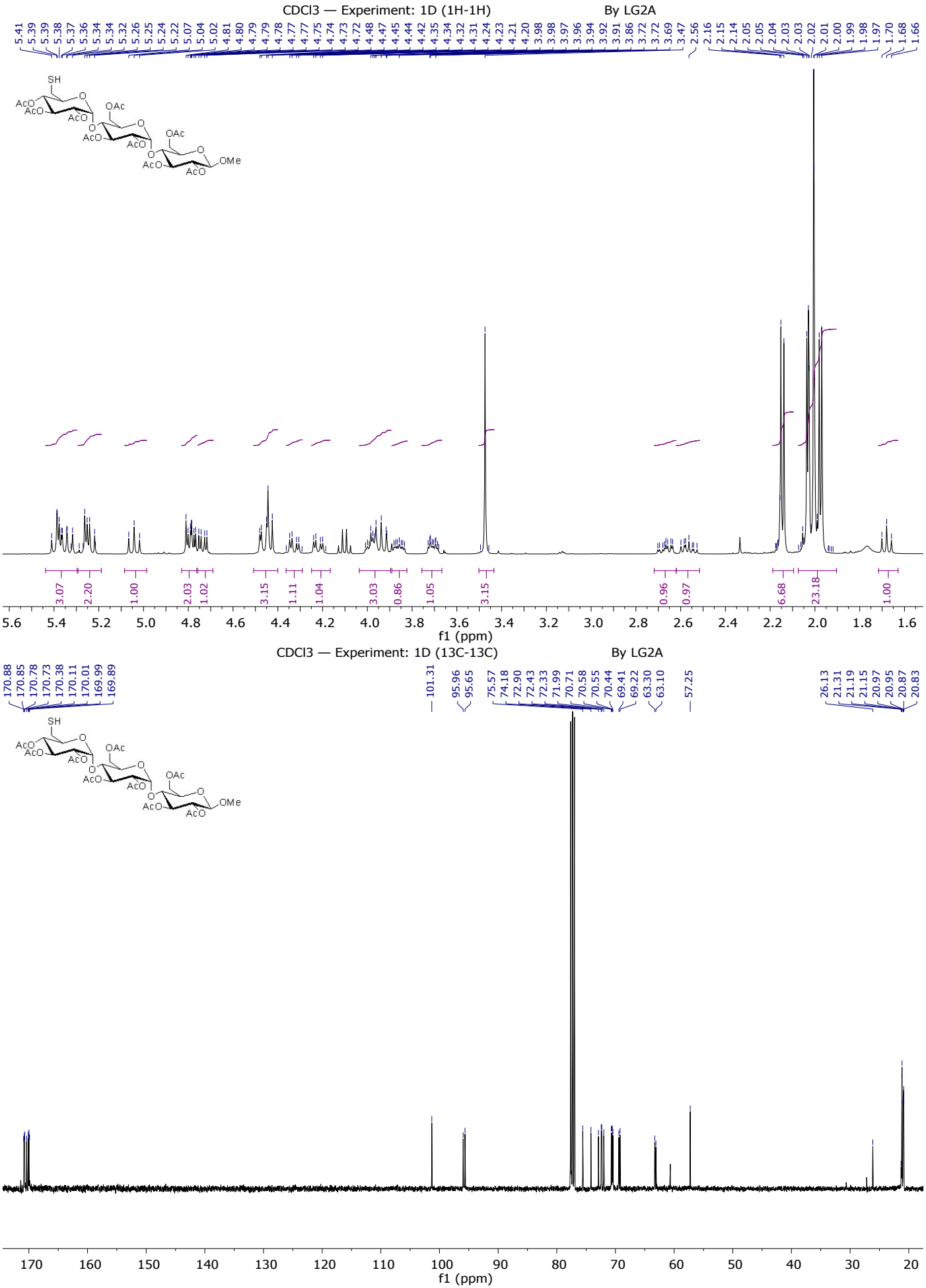


^{1}H (top) and ^{13}C (bottom) NMR spectra of **37**

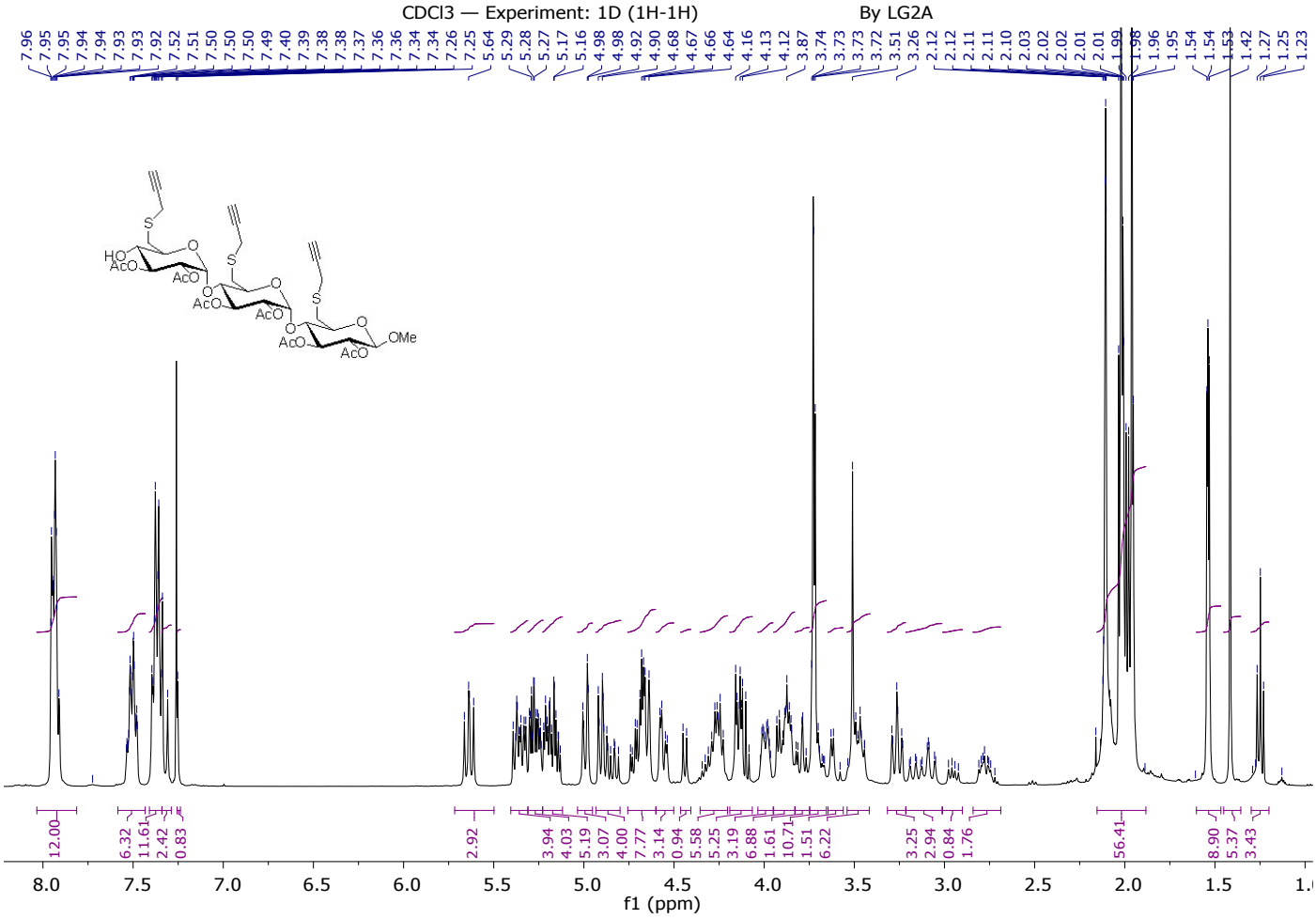


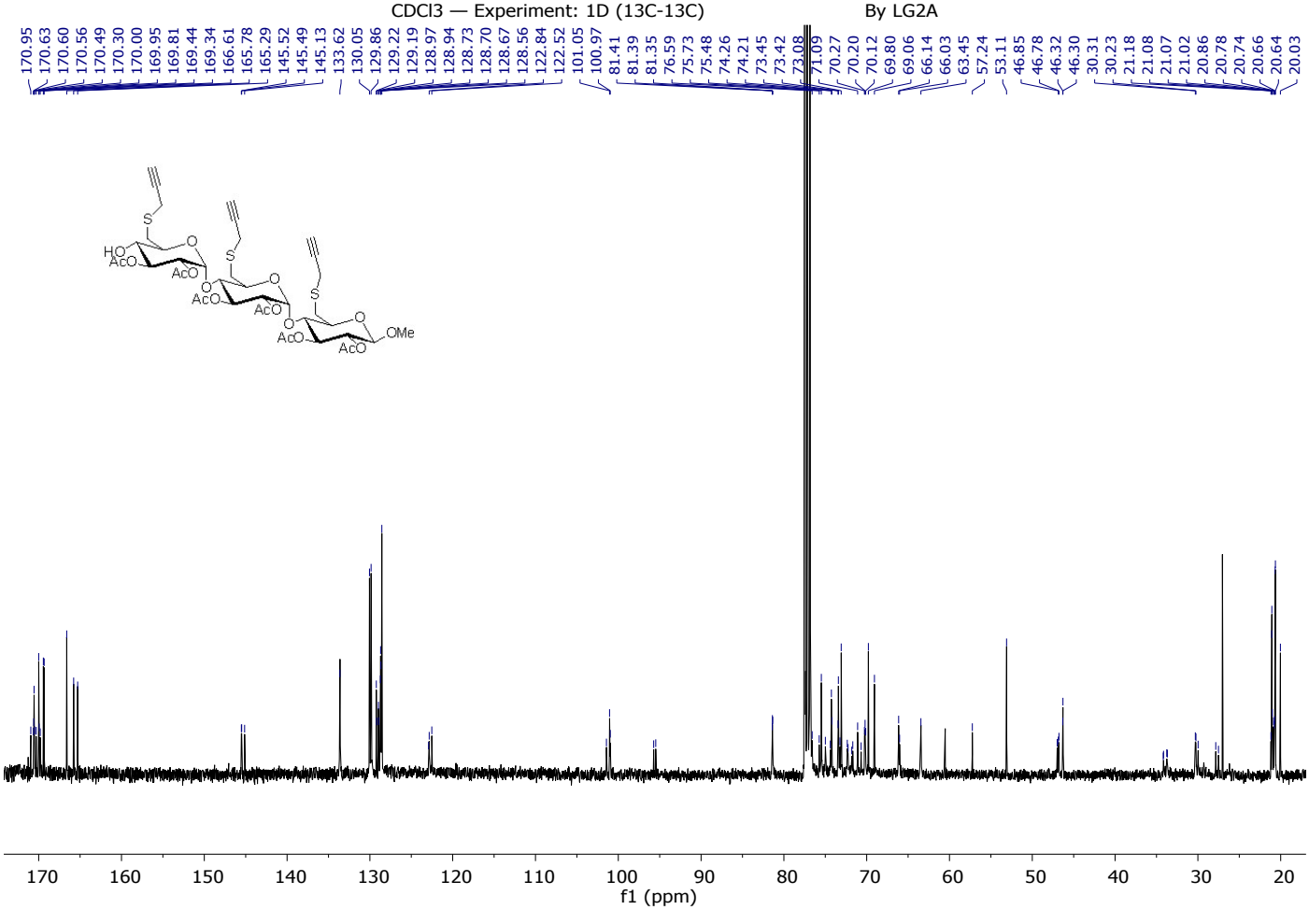


^{1}H (top) and ^{13}C (bottom) NMR spectra of **38**

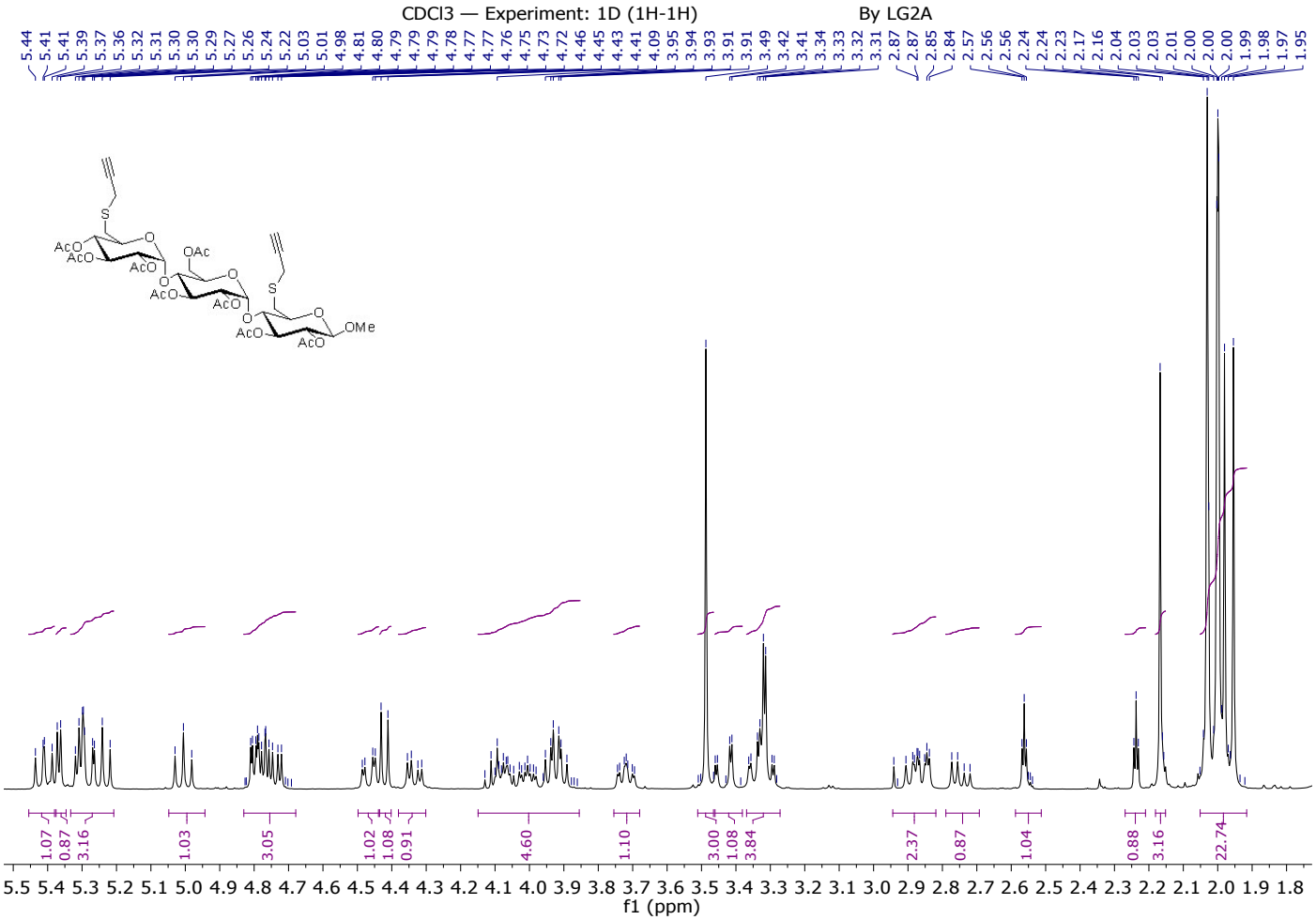


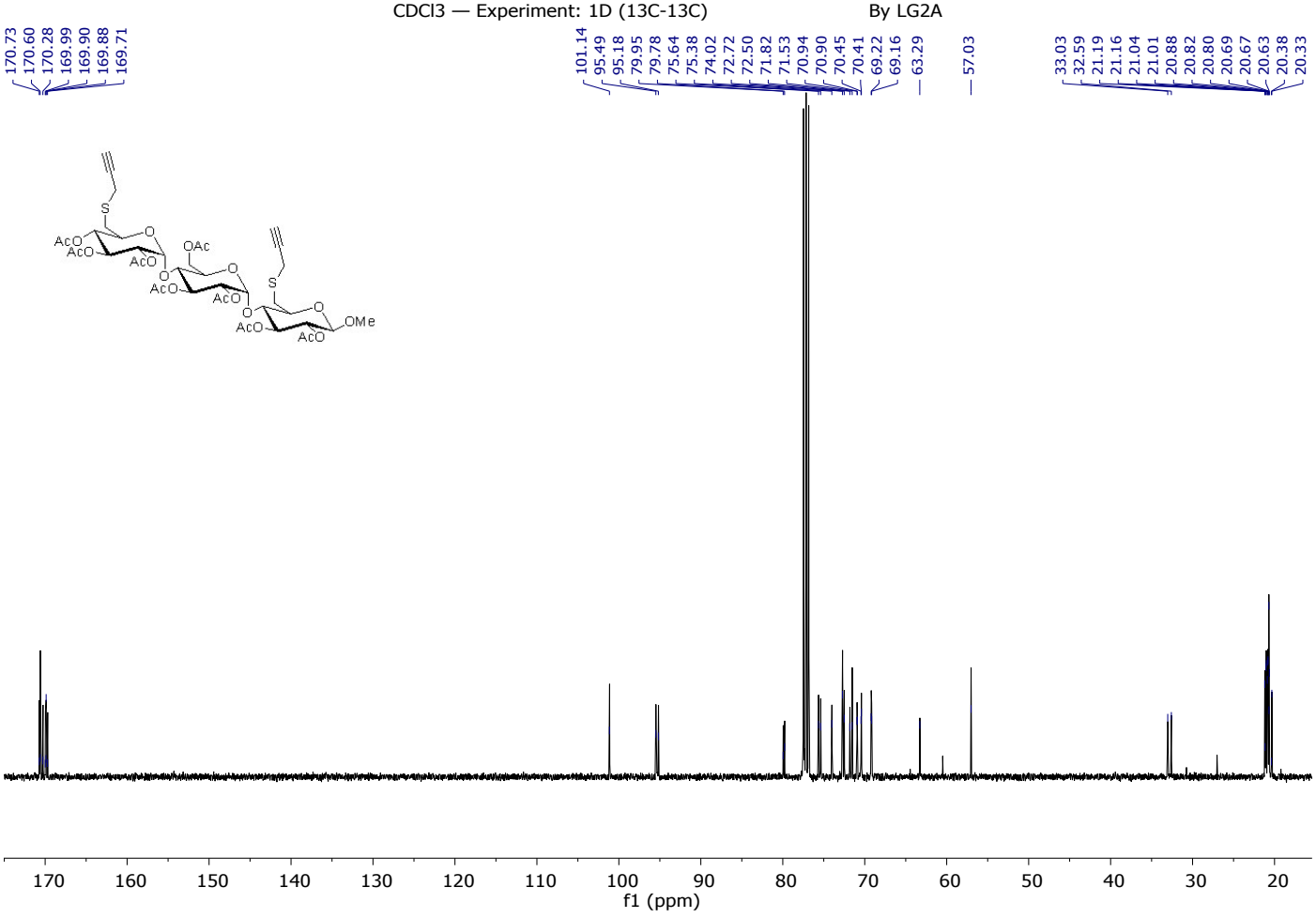
^{1}H (top) and ^{13}C (bottom) NMR spectra of **39**



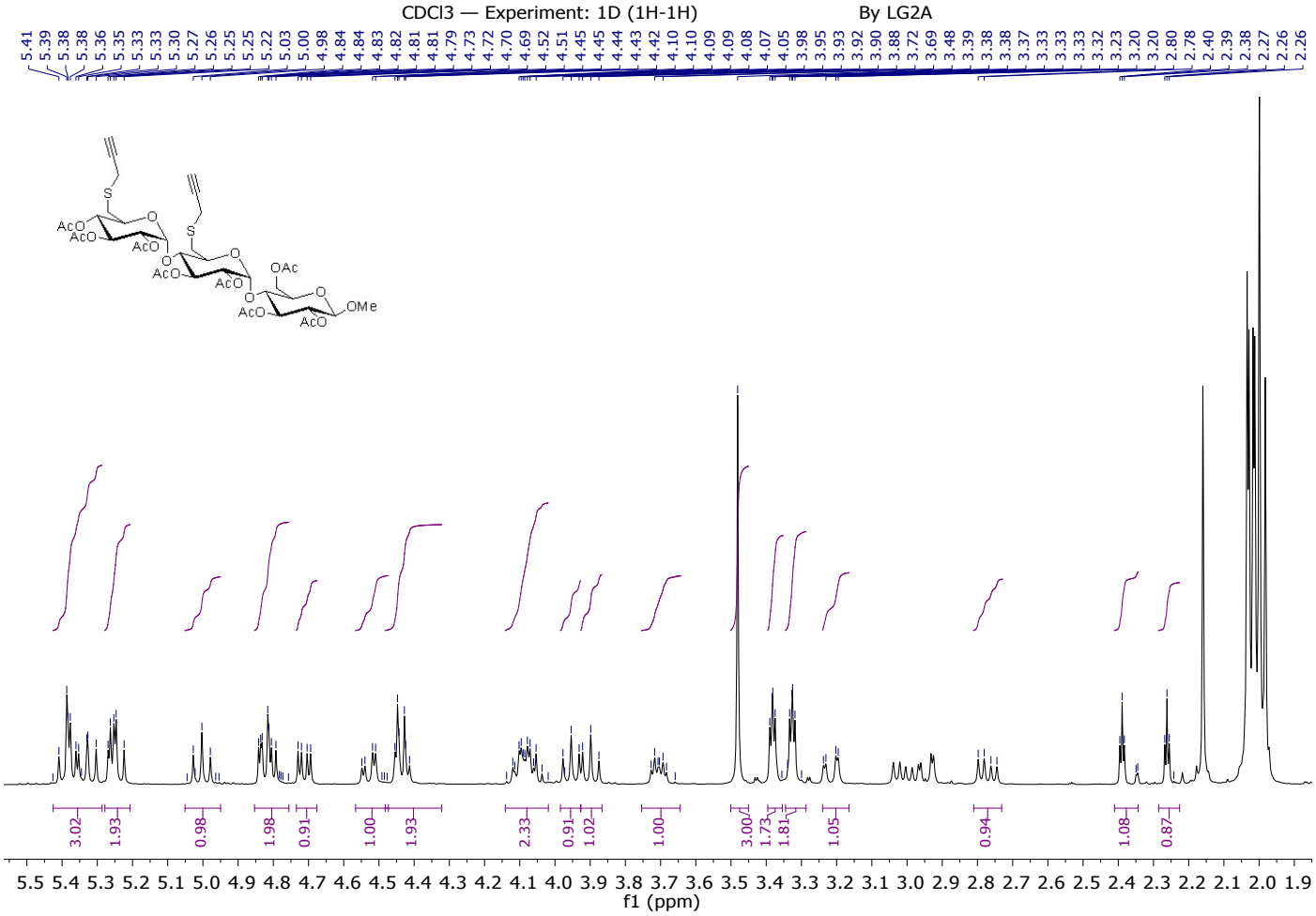


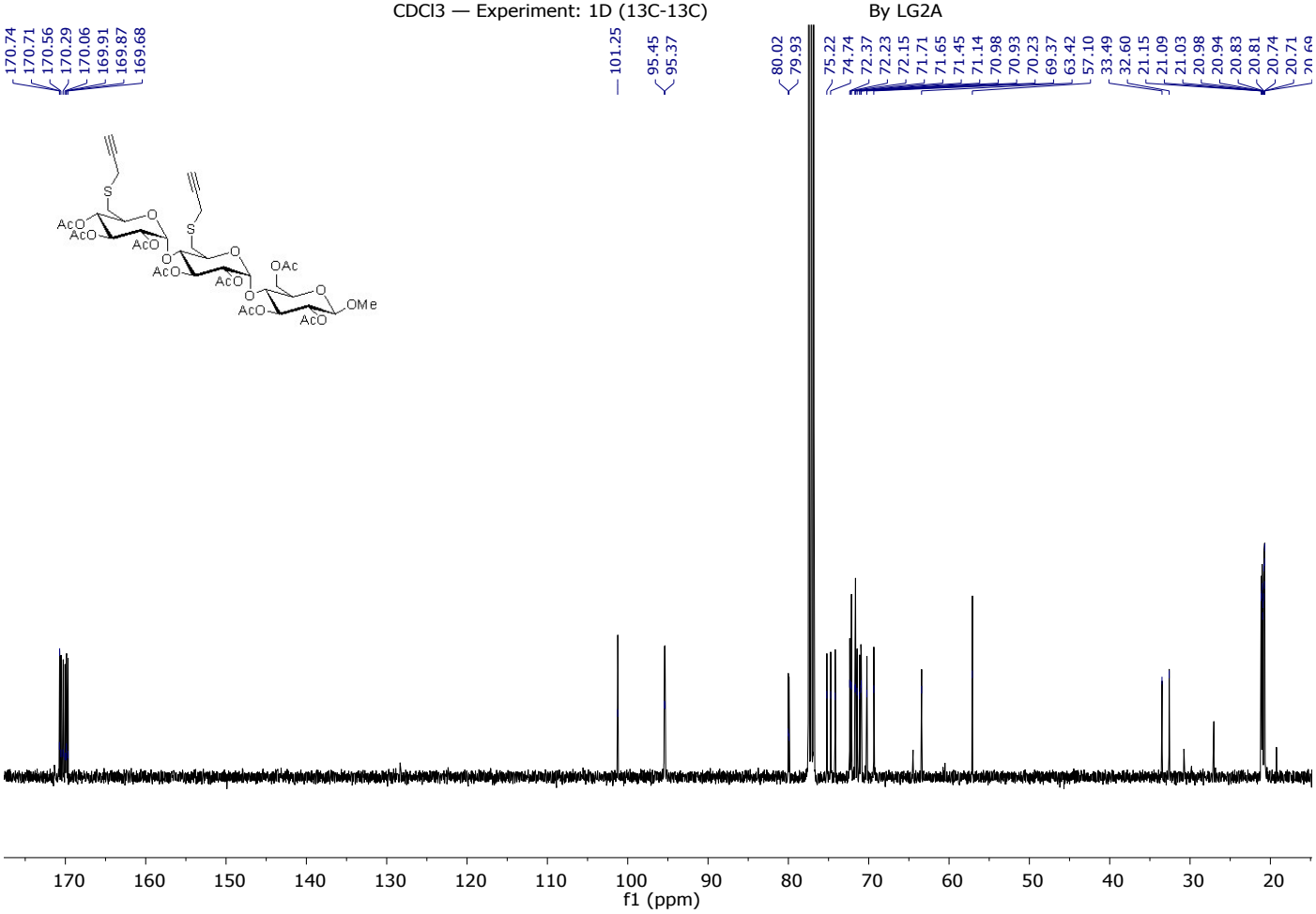
^{1}H (top) and ^{13}C (bottom) NMR spectra of **40**



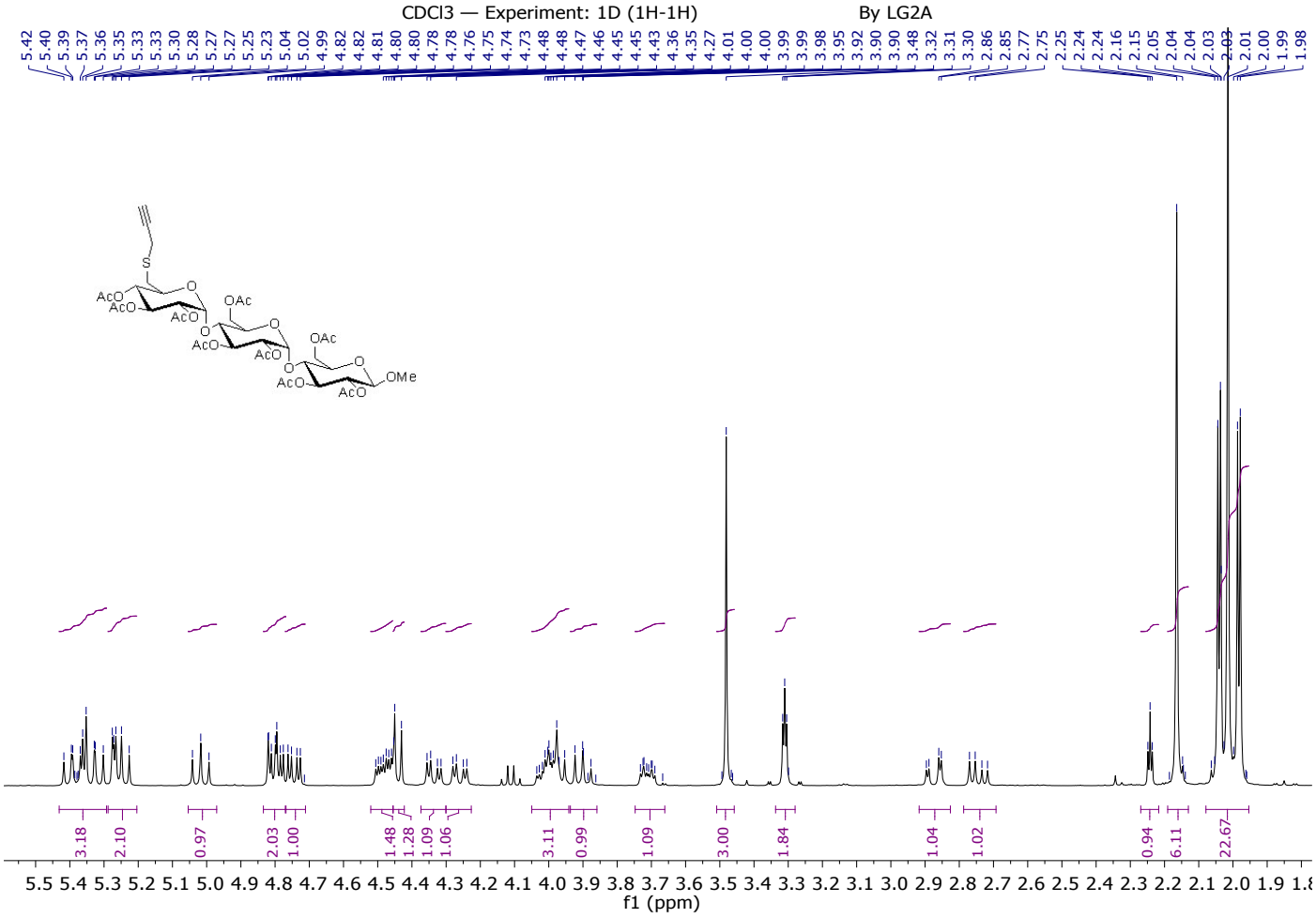


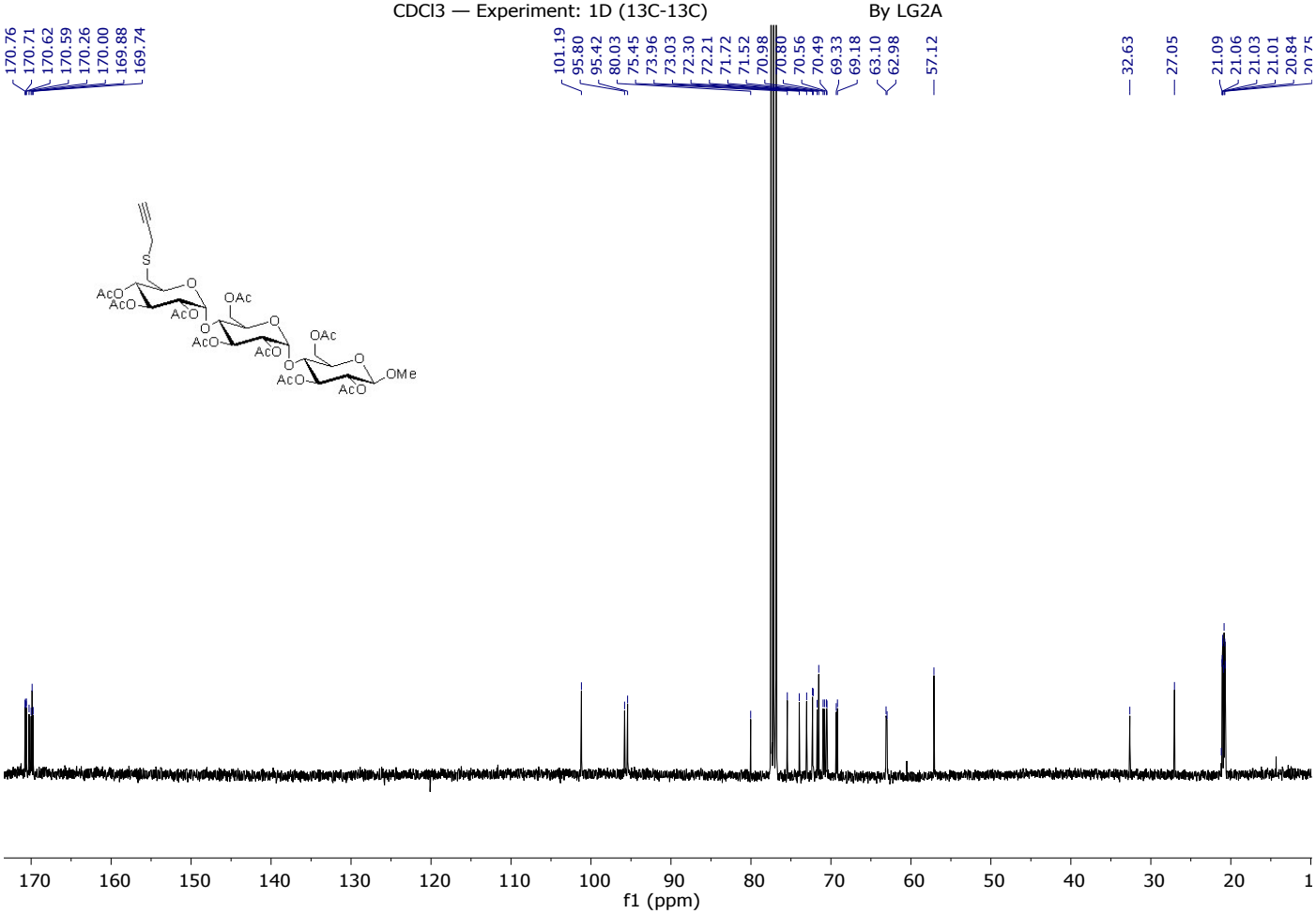
^{1}H (top) and ^{13}C (bottom) NMR spectra of **41**



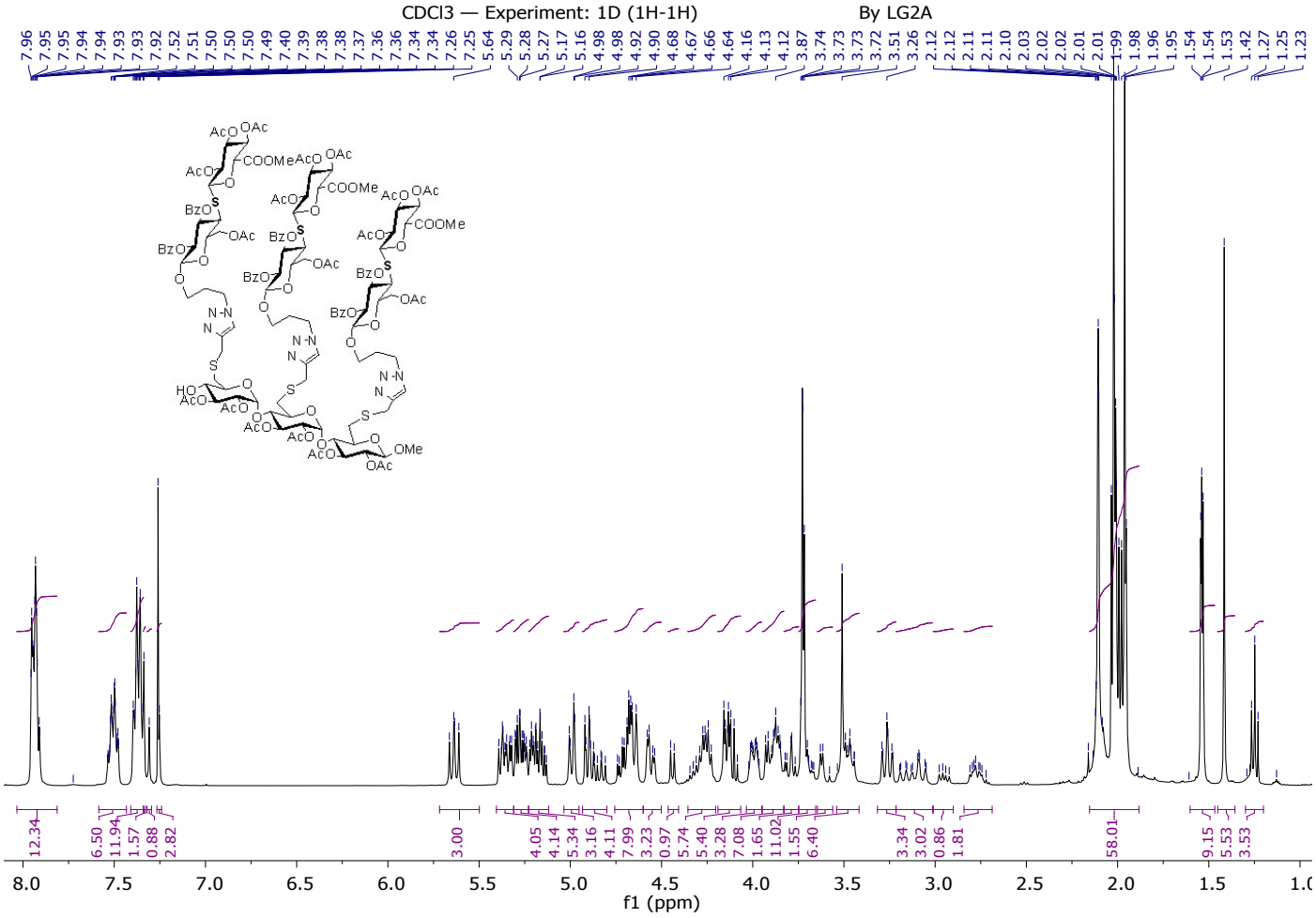


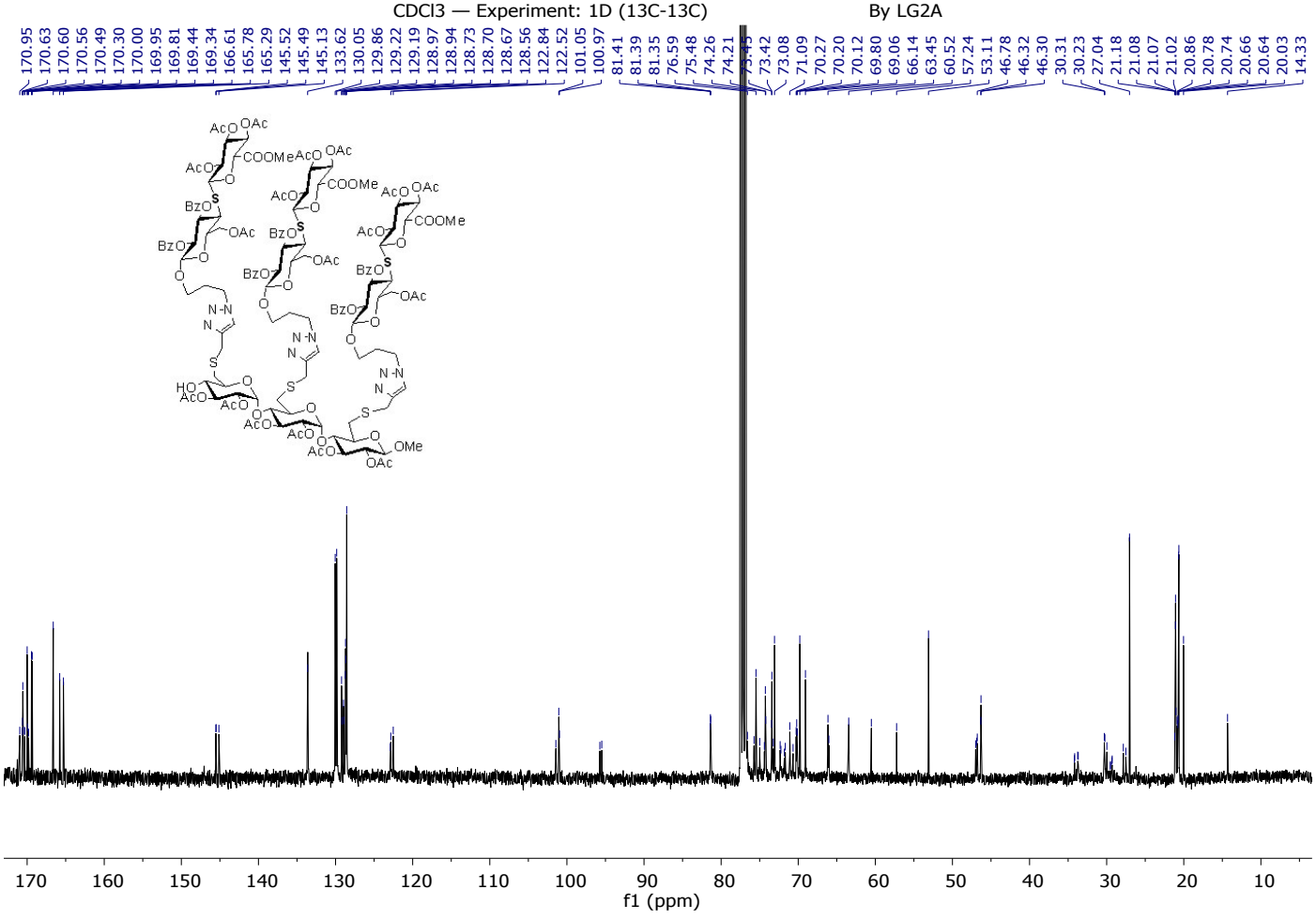
^{1}H (top) and ^{13}C (bottom) NMR spectra of **42**



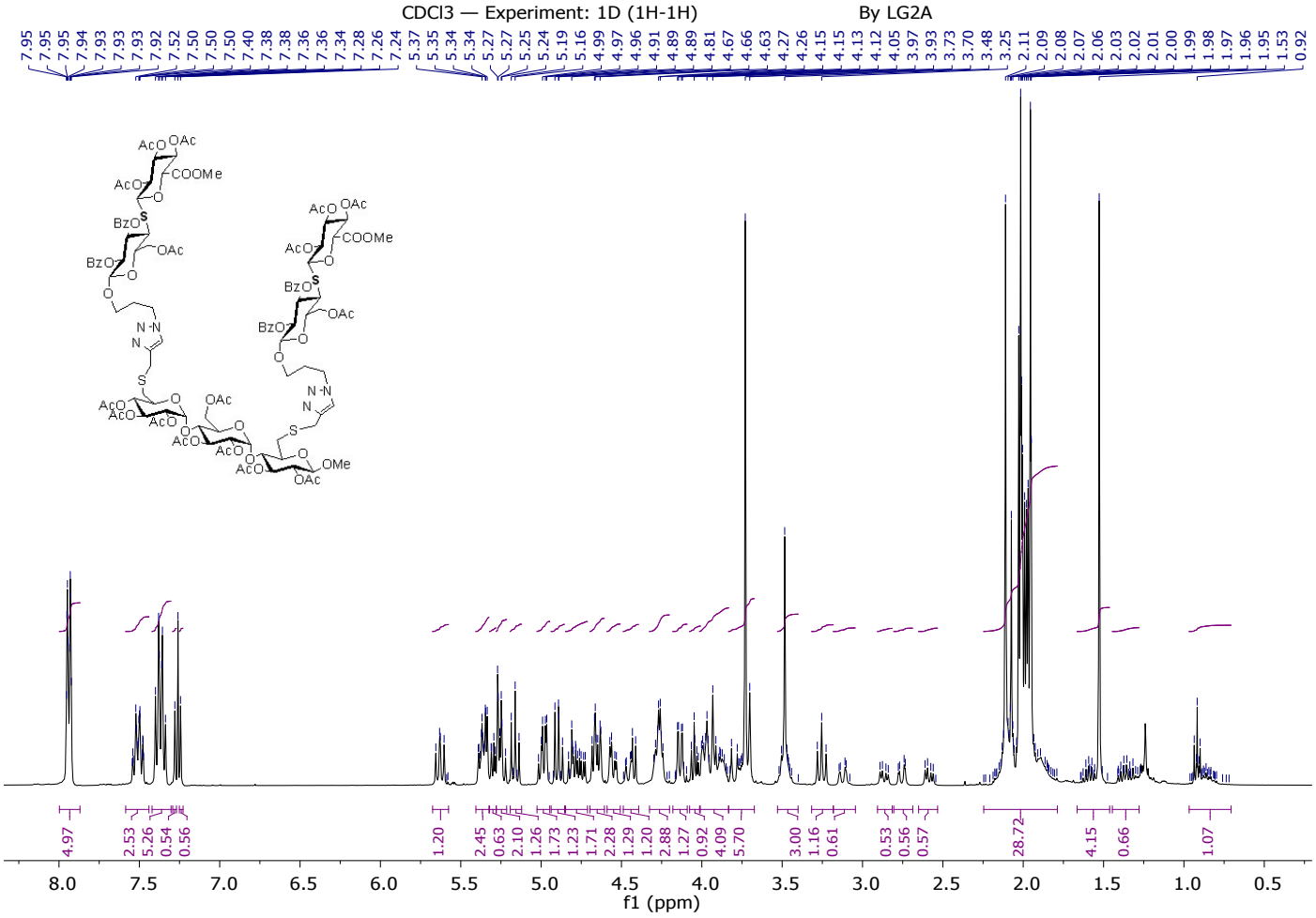


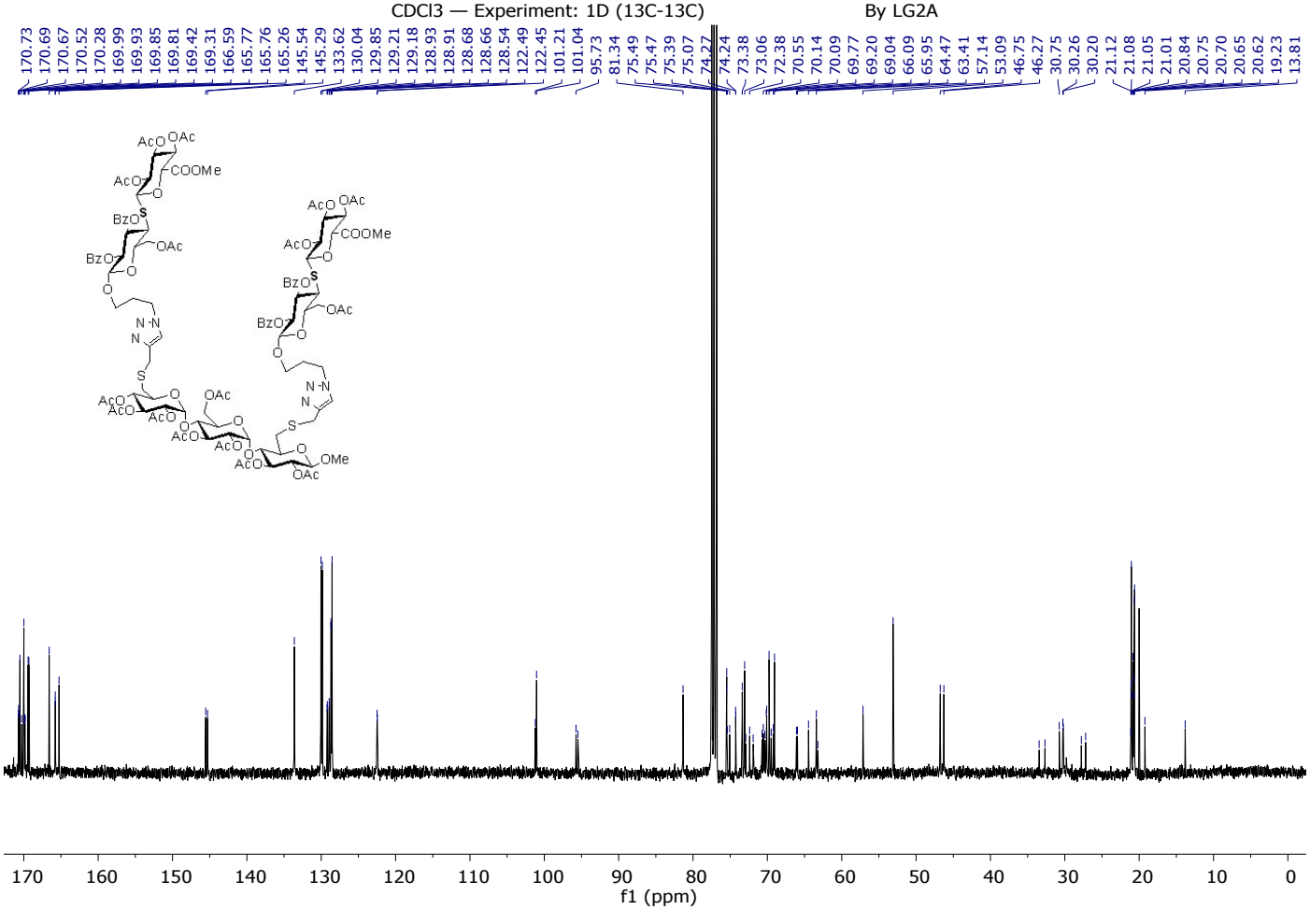
^{1}H (top) and ^{13}C (bottom) NMR spectra of **43**



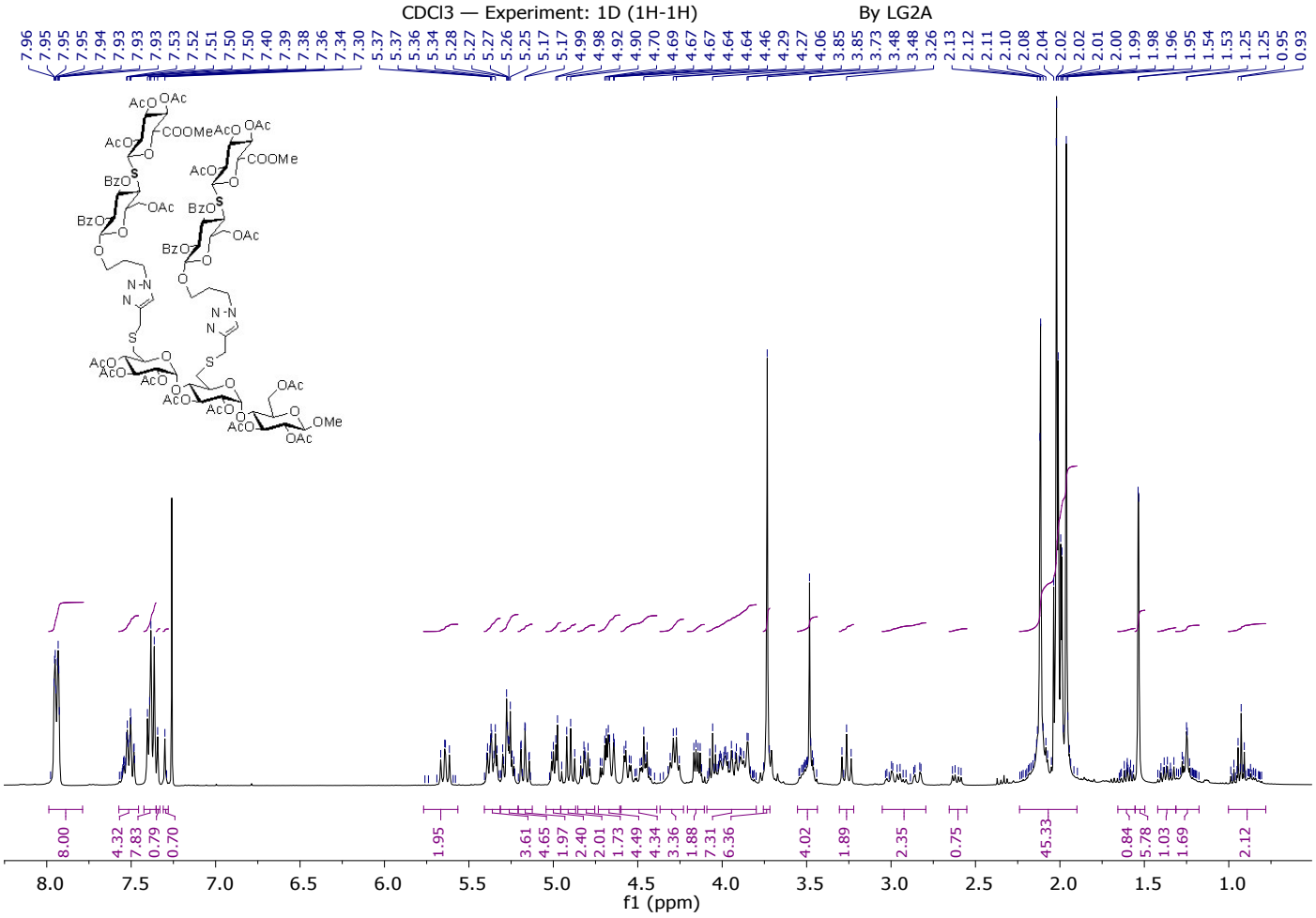


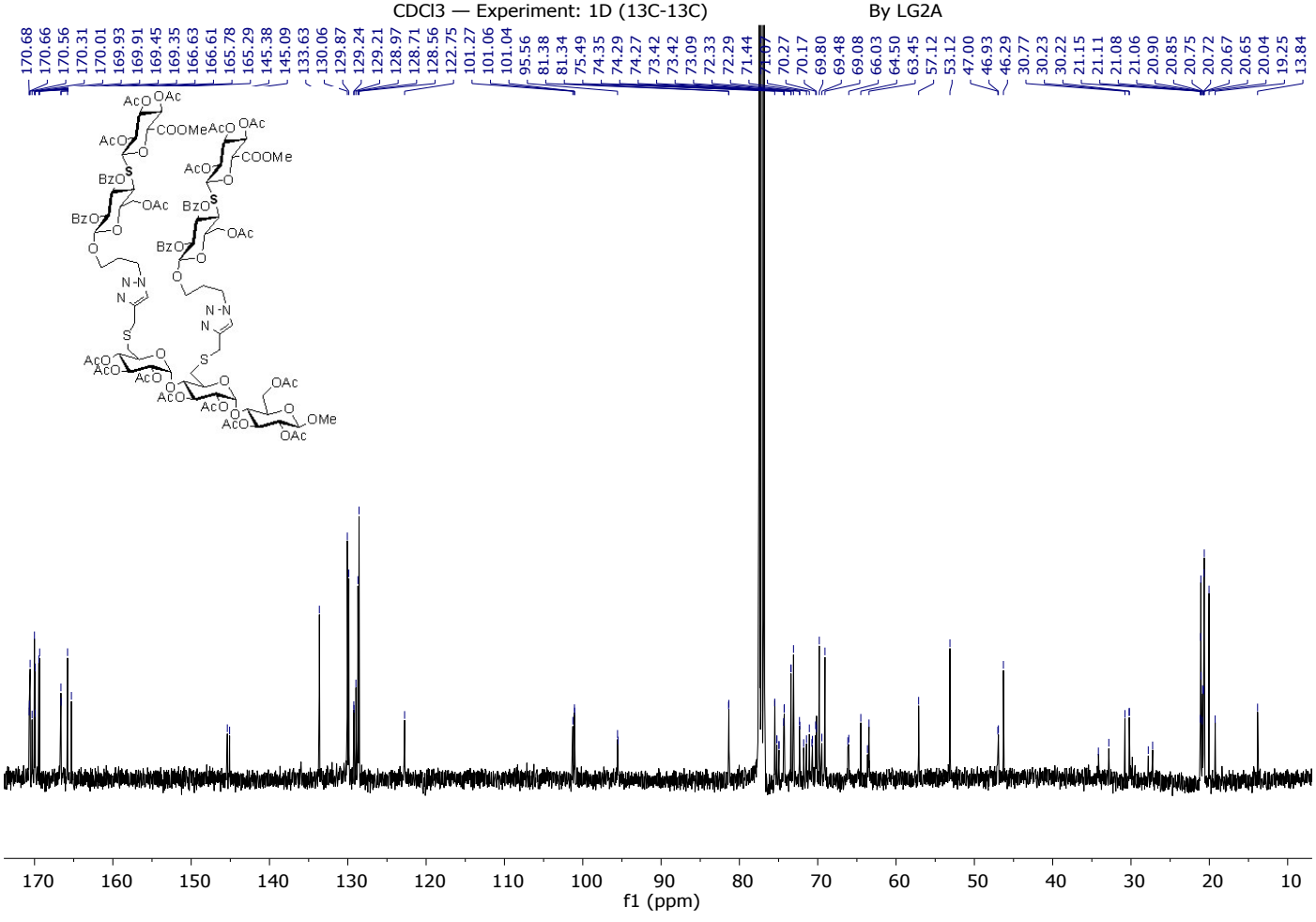
^{1}H (top) and ^{13}C (bottom) NMR spectra of **44**



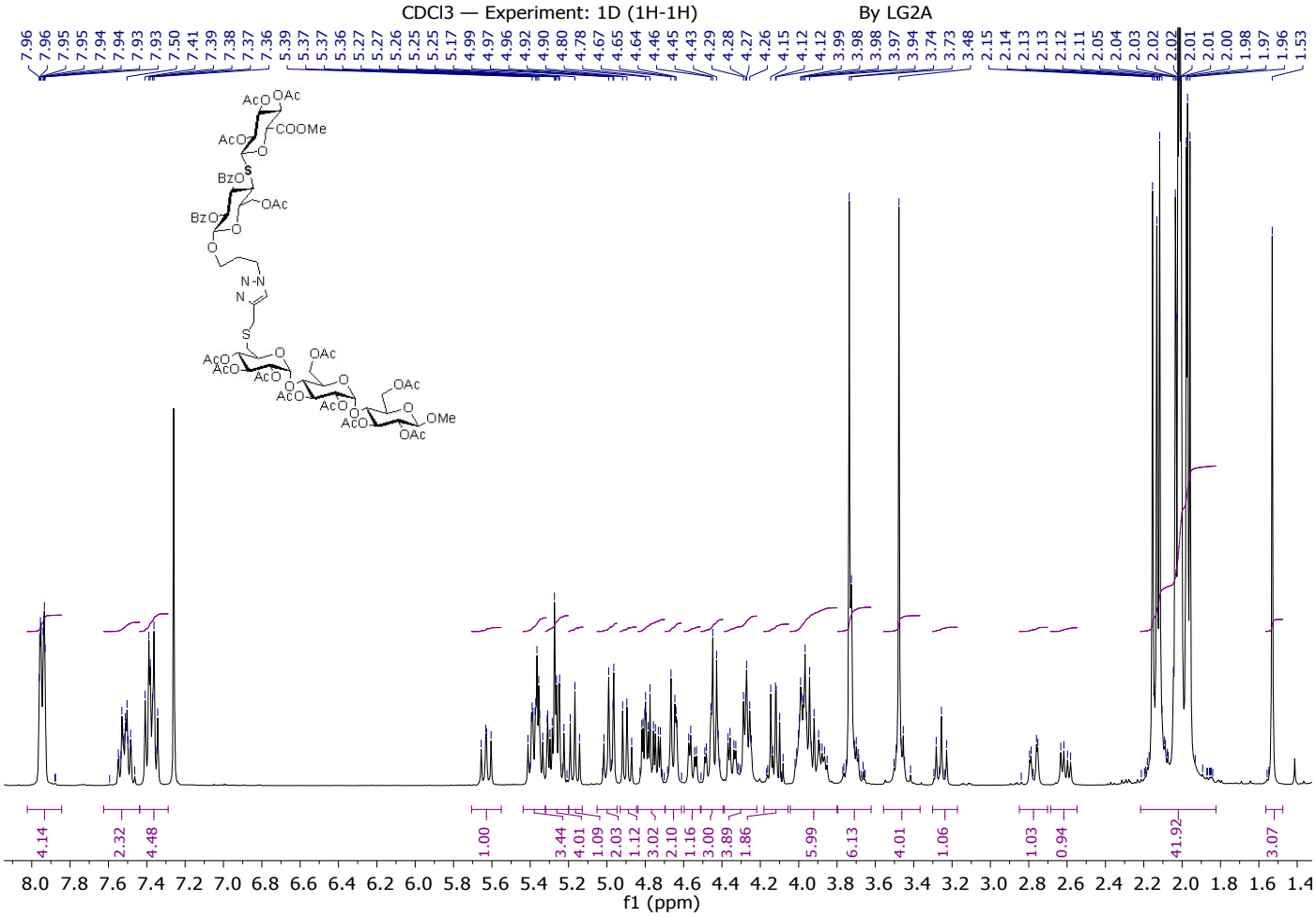


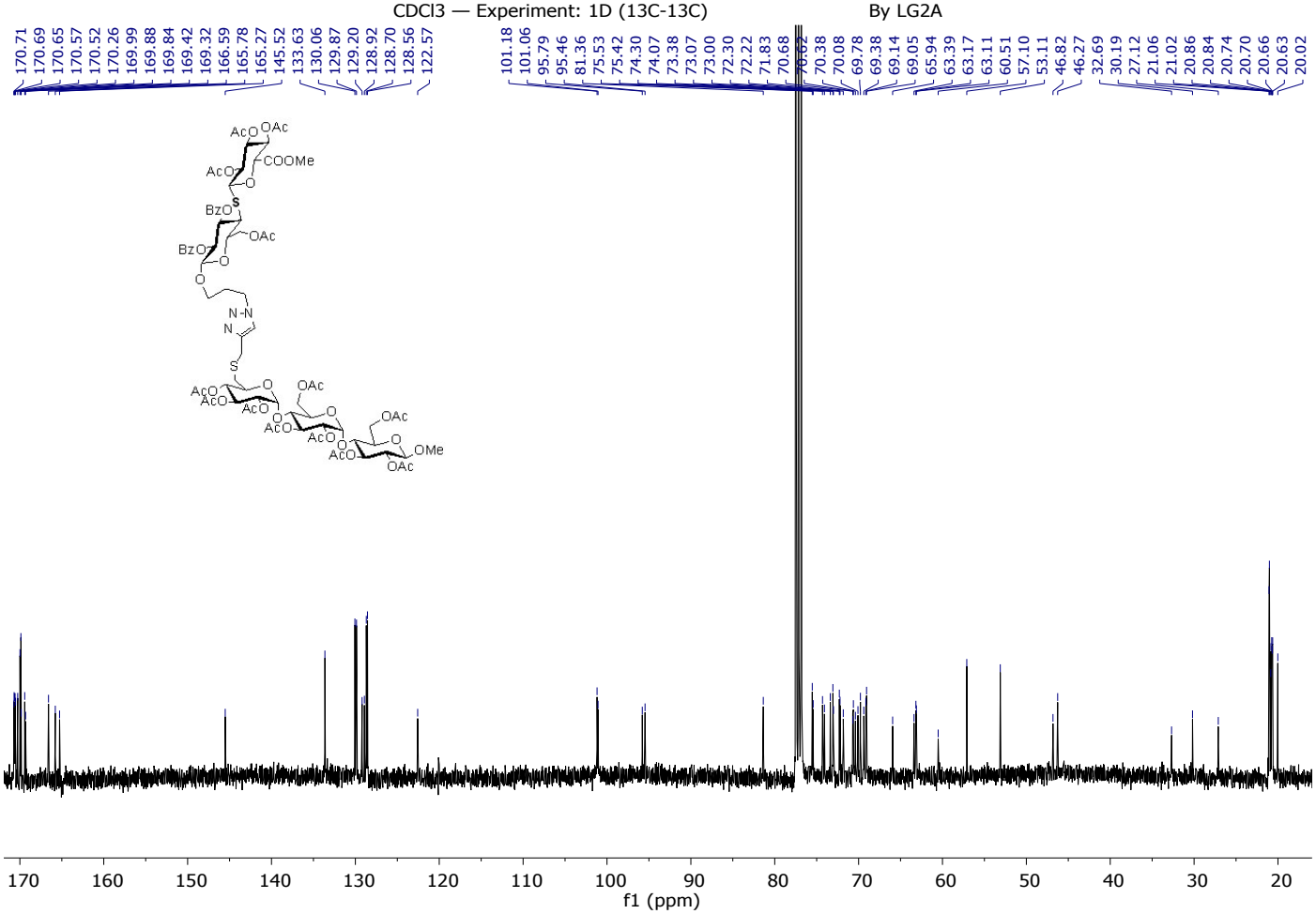
^{1}H (top) and ^{13}C (bottom) NMR spectra of **45**



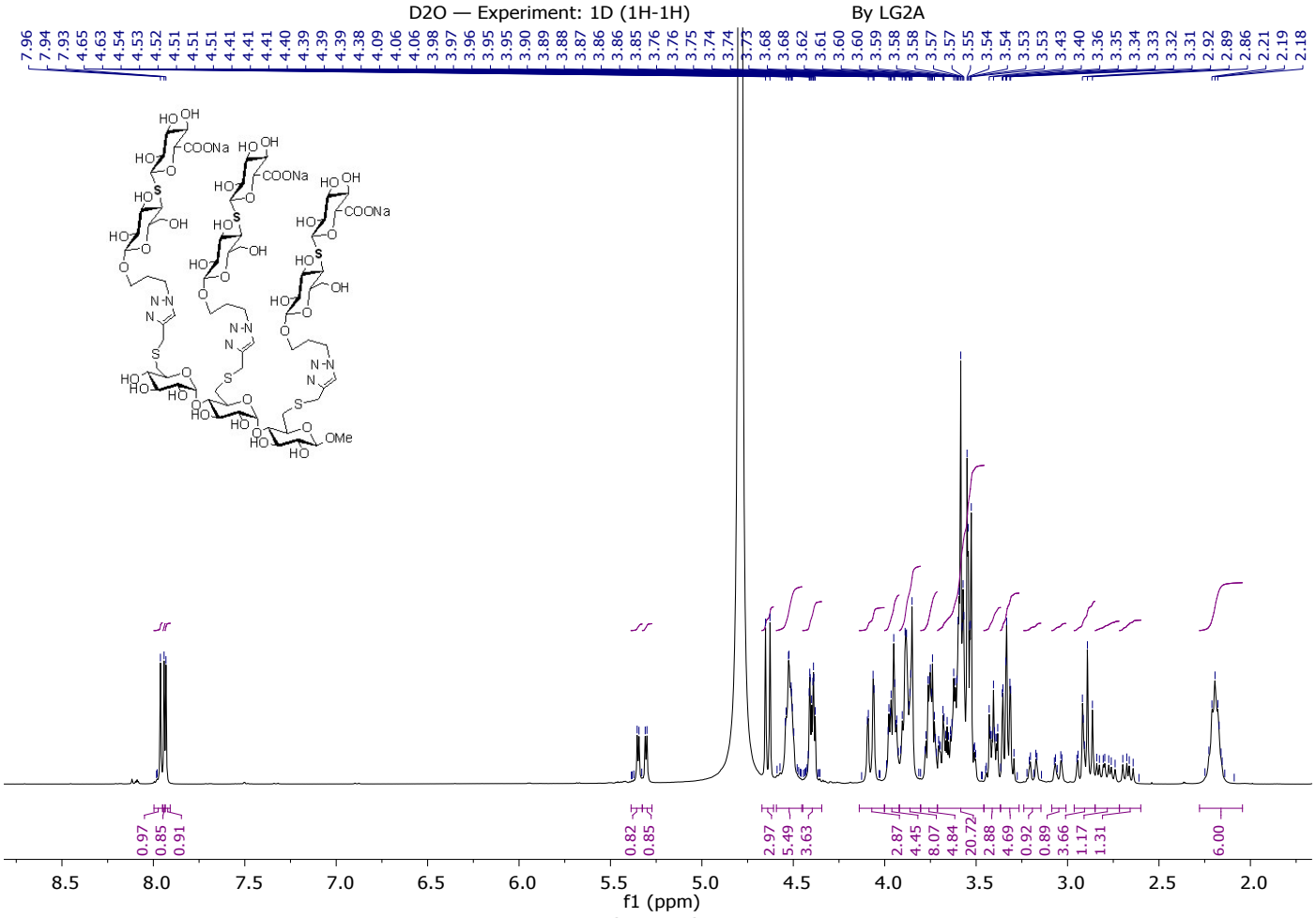


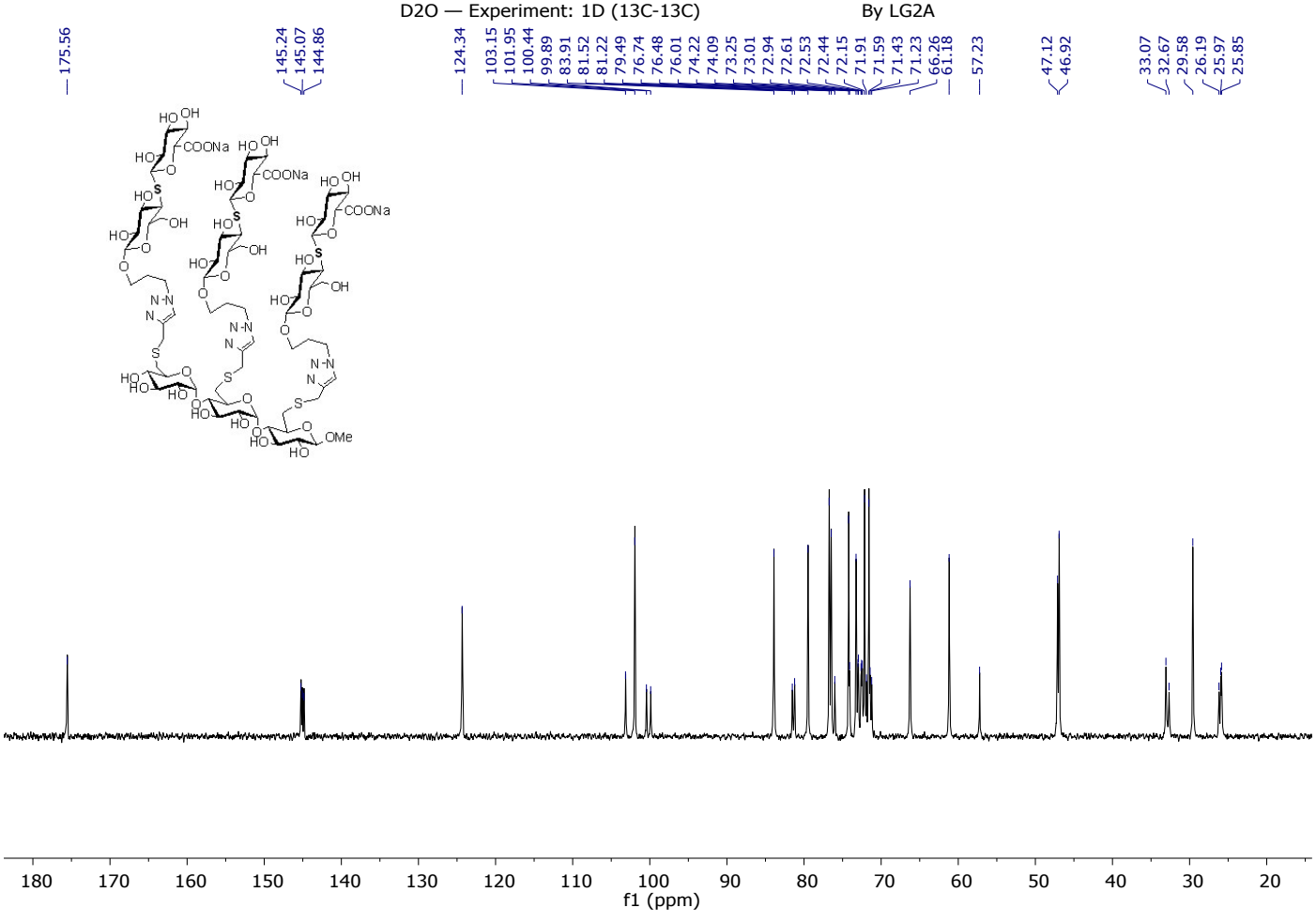
^{1}H (top) and ^{13}C (bottom) NMR spectra of **46**



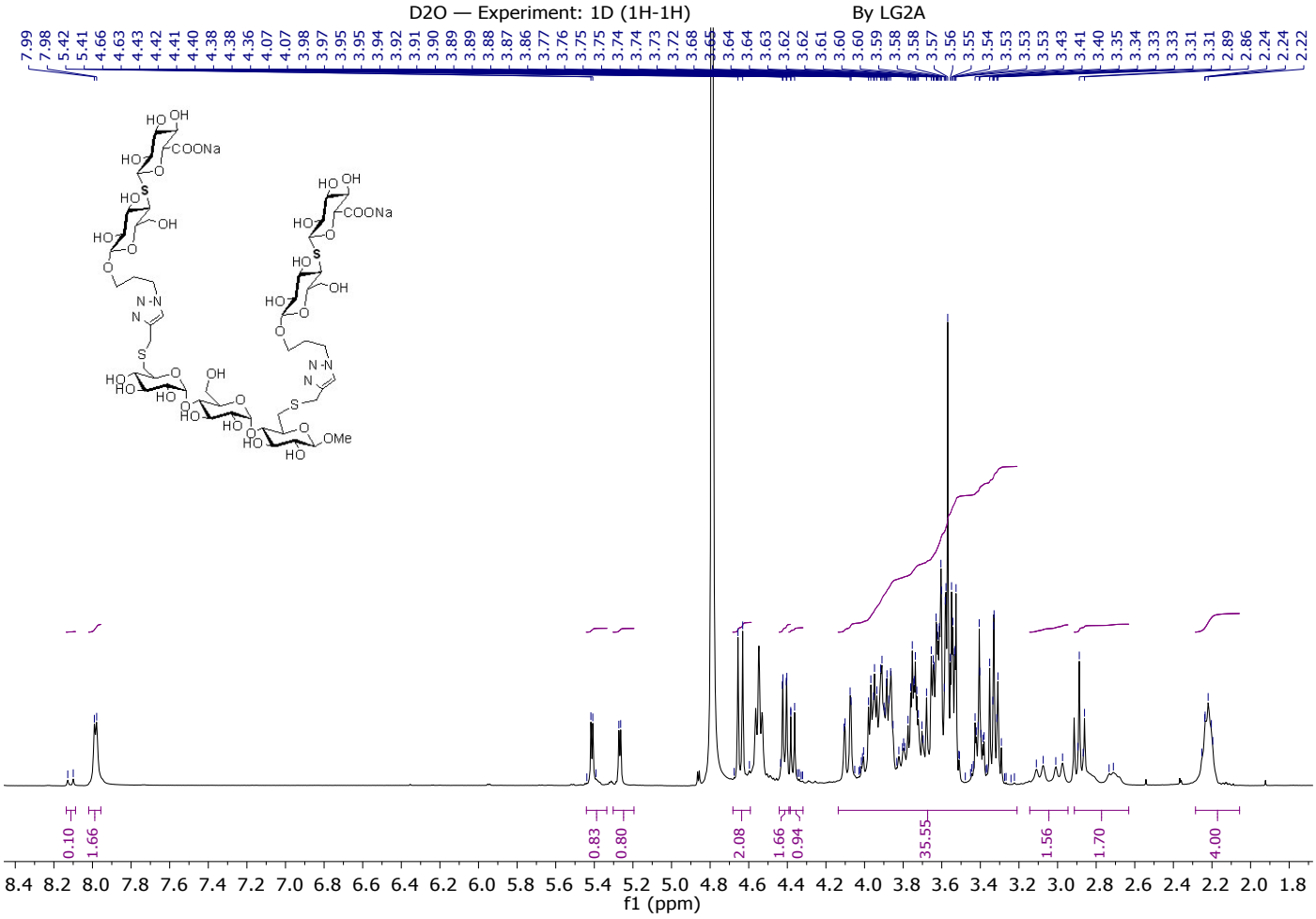


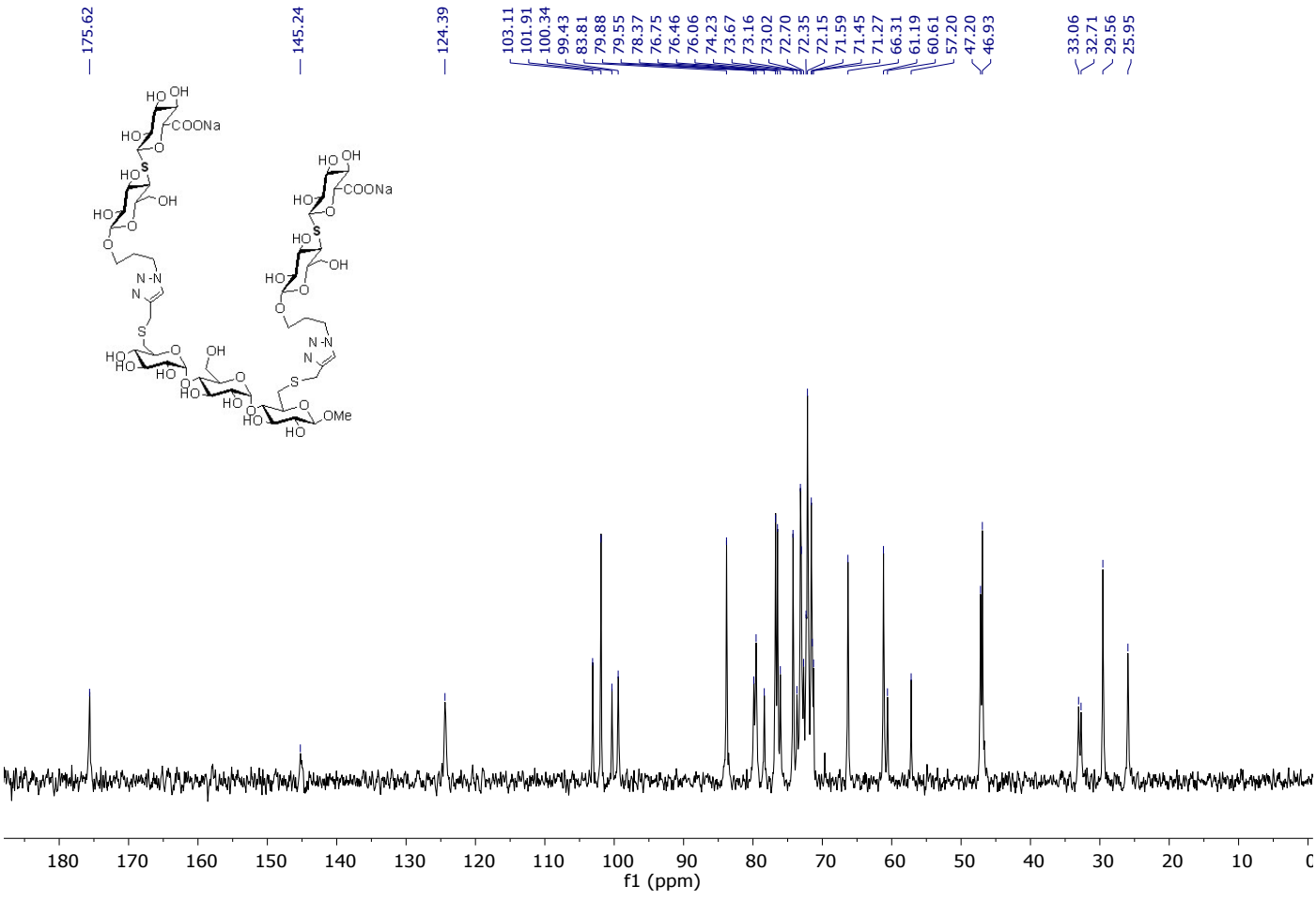
^{1}H (top) and ^{13}C (bottom) NMR spectra of **47**



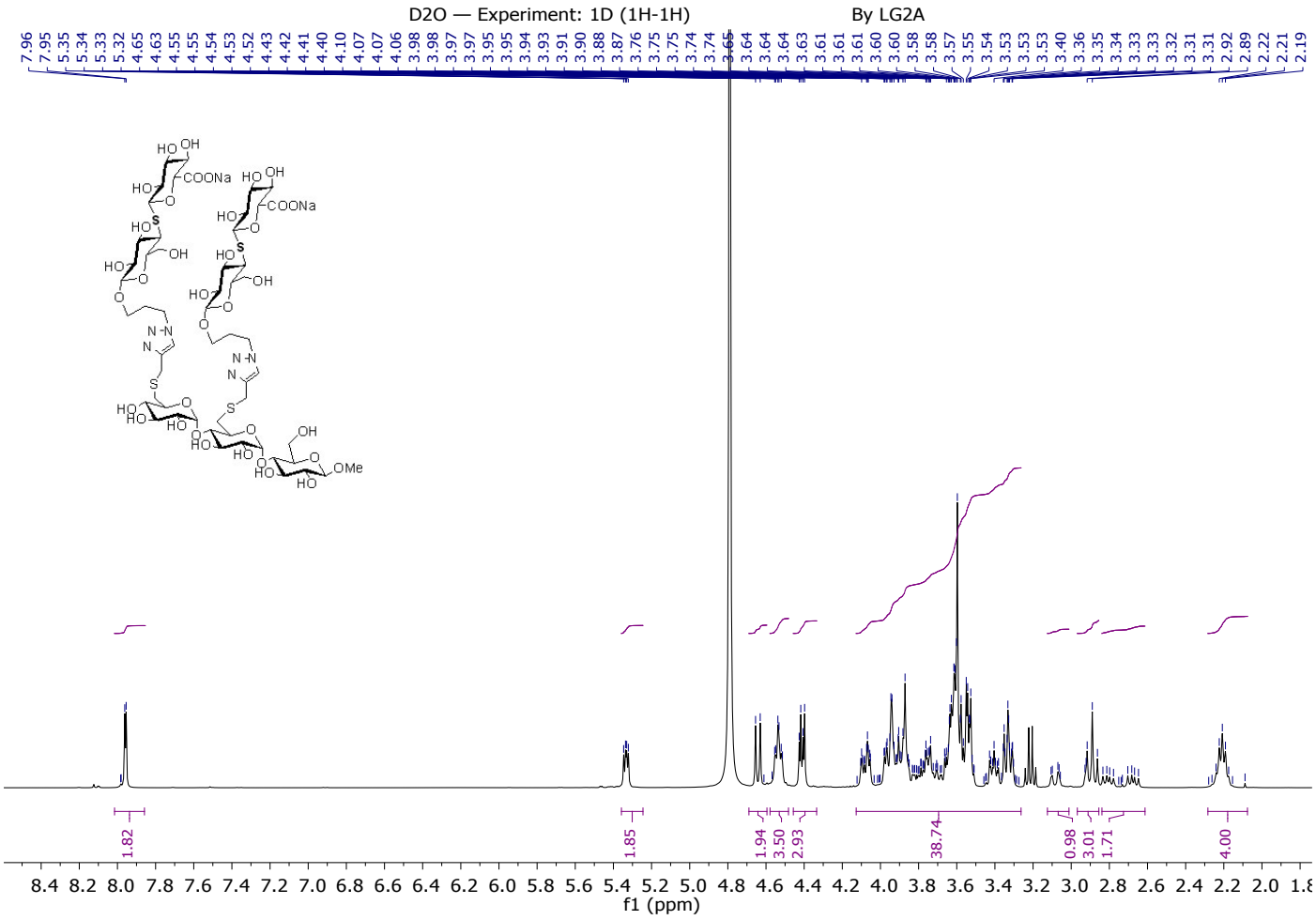


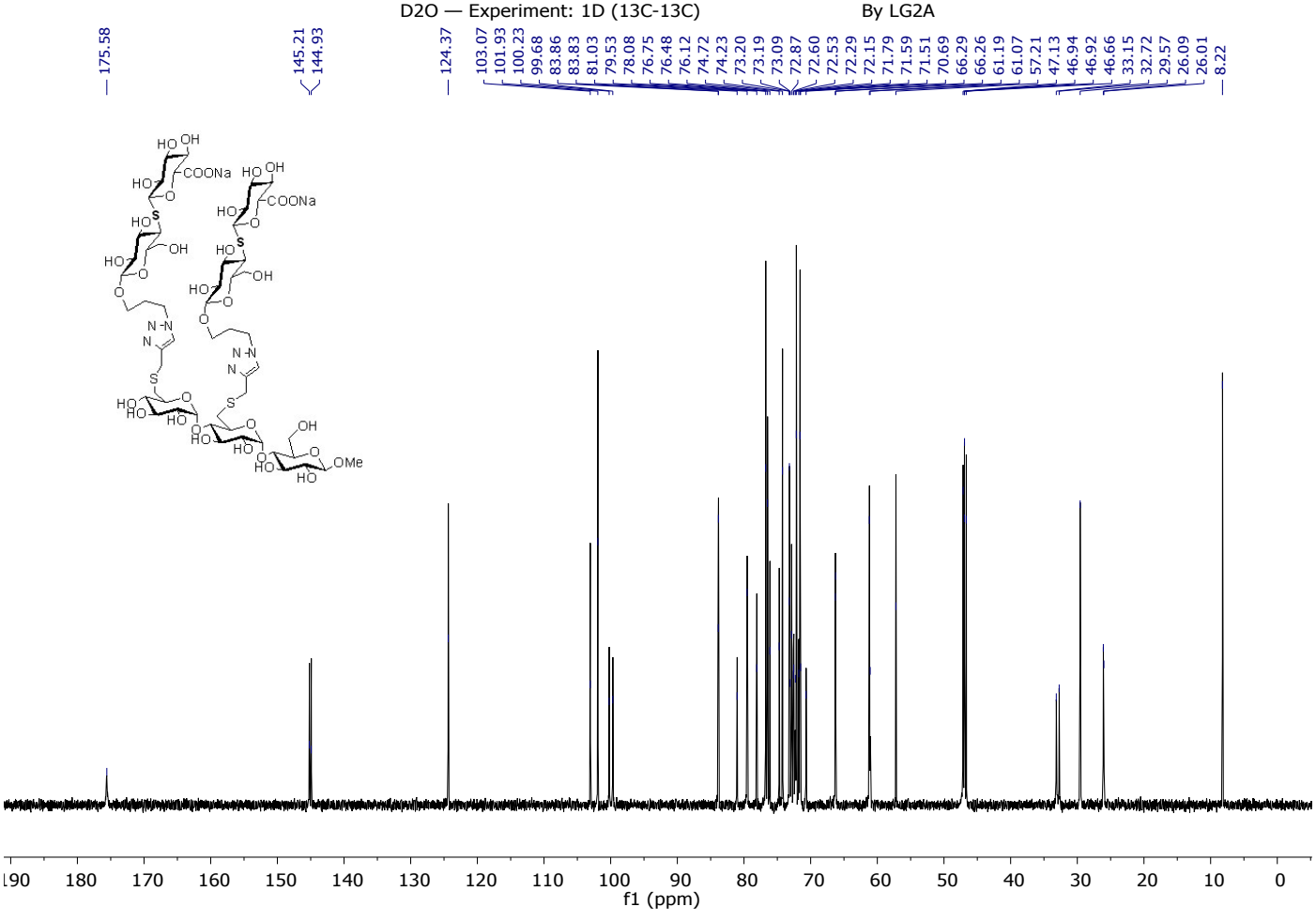
^{1}H (top) and ^{13}C (bottom) NMR spectra of **48**



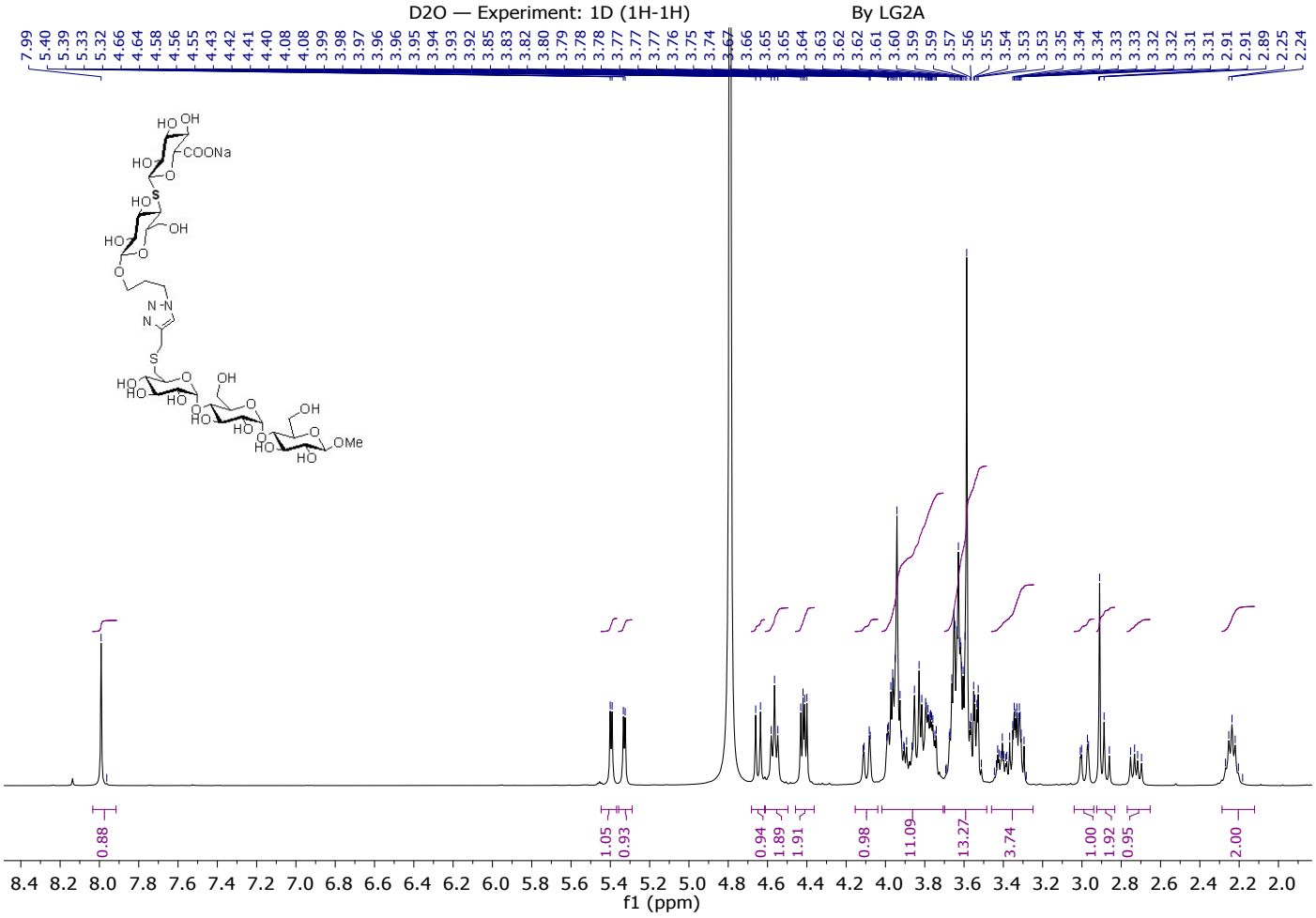


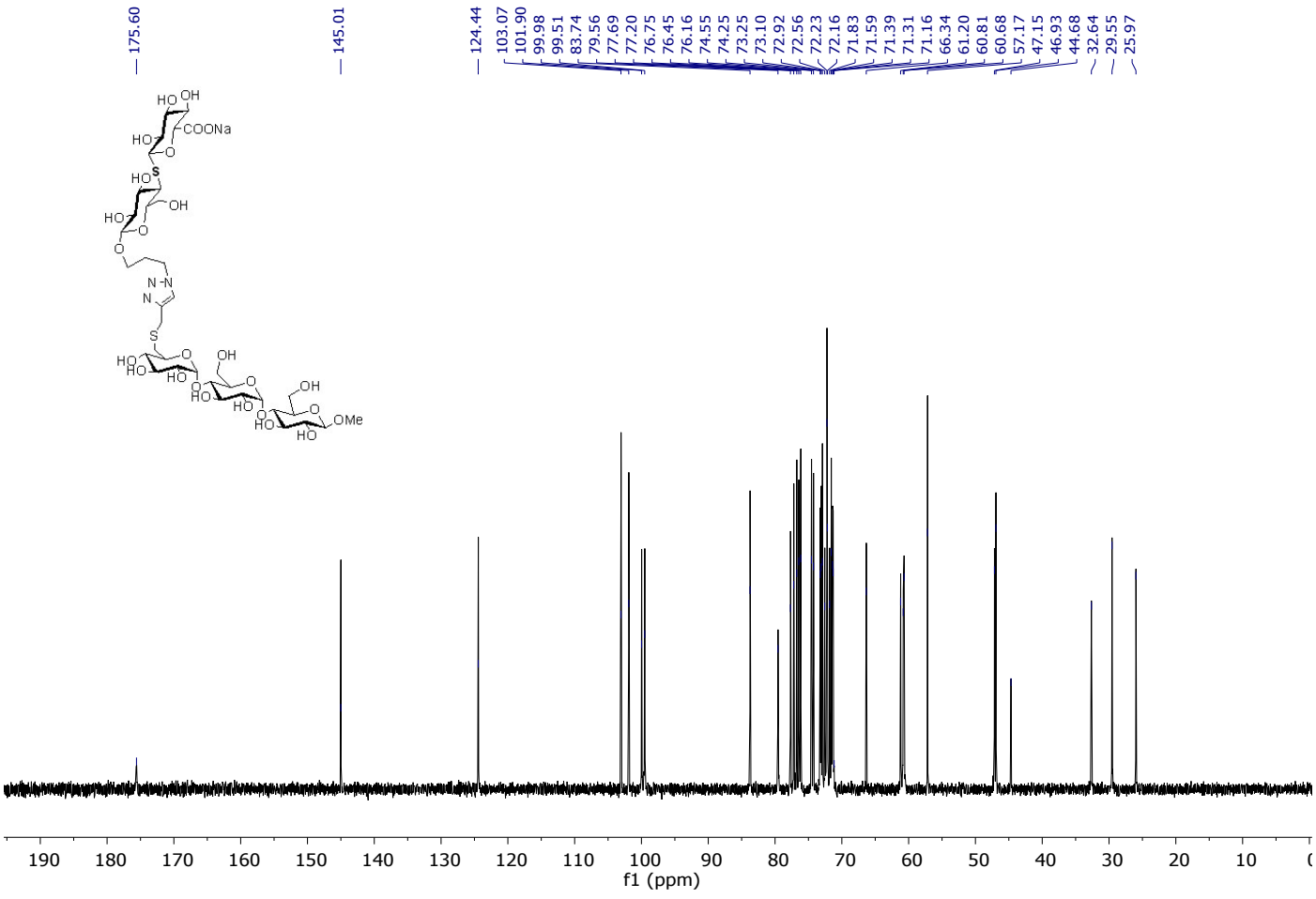
^{1}H (top) and ^{13}C (bottom) NMR spectra of **49**





^{1}H (top) and ^{13}C (bottom) NMR spectra of **50**





^{1}H (top) and ^{13}C (bottom) NMR spectra of **51**